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Assessment of Atmospheric Emissions from Petroleum Refining: Volume 4 Appendices C, D, and E

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Austin, TX

Prepared for

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16. ABSTRACT The report gives results of a 3-year program to assess the environmental impact of petroleum refining atmospheric emissions. This volume contains Appendices C. D. and E. Appendix C presents the quality assurance program and a statistical analysis of the emissions data. It describes quality control procedures for screening, sampling, analyzing, species identification, and data validation. It discusses the accuracy and precision of the various data types. Appendix D describes the procedures used to develop a detailed environmental assessment of refineries. Refinery emission rate data were used to predict ambient pollutant levels near a model refinery. The environmental effects and the potential hazard to the public are discussed. Appendix E is a detailed review and evaluation of pollution control technology. The state-of-the-art of fugitive and process emission controls in refineries is reviewed. Available controls are described. Control technologies used in related industries are examined for potential applicability in the refining industry.

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1.0 OVERVIEW OF QUALITY ASSURANCE PROGRAM

From the beginning of this program, the importance of a comprehensive quality assurance effort was emphasized. All phases of the sampling and analysis effort from experimental design to data reduction included specific quality control procedures. The quality control programs were continuously reviewed by Radian's Quality Assurance Director who reported his findings to the Project Technical Director and Program Manager. There were two major objectives of the QA effort:

- to identify problems as they occurred in the field, and
- to measure and document occurring levels of accuracy and precision of all measurements.

Quality control guidelines were developed to be both cost effective and adequate to insure credible data. The quality assurance program for the sampling and analysis activities included the following elements:

- formatted data collection forms for direct keypunching of data recorded in the field,
- repeated sampling of individual sources with the same and different sampling teams and sampling equipment,
- sampling and subsequent analysis of standard gas mixtures,

- continuous sample runs over an eight-hour period,

- daily testing of screening devices on the same sources,

- multiple screenings of the same devices by different engineers, and

- replicate sample analysis and blind standard analysis in the laboratory.

Quality control procedures for screening, sampling, analyses, speciation, and data validation were originally described in the technical proposal for the program. Specific quality control charts and forms and modified QC procedures were implemented at Refinery "E" in November 1977, and used through the remainder of the program.

This appendix presents the various types of quality control data collected during the program. The statistical analysis of the data and the accuracy and precision of the various data types are discussed. Section 6.0 describes statistical models and procedures used in summarizing and analyzing the data collected during the program.

The quality assurance effort also included many other procedures which have been discussed in describing the sampling and analysis methodology in Appendix A. Specific calibration procedures used on all equipment are discussed in the methodology sections of Appendix A.

2.0 QUALITY CONTROL FOR BAGGABLE HYDROCARBON MEASUREMENTS

This section describes the quality control procedures implemented during the analysis of samples for methane and nonmethane hydrocarbon from process valves, pump seals, compressor seals, flanges, relief valves, and drains. A significant amount of the total quality assurance effort went into this area because the sampling procedure had not been previously validated under field conditions and because of the extreme variability of leak rates found from these sources.

The quality control procedures discussed here include laboratory blind standards analysis, repeatability of the total hydrocarbon (THC) analysis, recovery studies of the sampling train, and reproducibility of the sampling/analysis from a given source.

2.1 Laboratory Standard Analysis

Regularly scheduled analyses of blind standards were used to evaluate the THC daily calibration as well as the stability of the calibration. The quality assurance protocol required at least one blind standard to be analyzed each week. The following standard gases were used for these checks:

Propane (NBS)	16.3 ppmv - 722 ppmv
Hexane	525 ppmv - 8,393 ppmv
Methane	103 ppmv - 433 ppmv
C_1 - C_6 Hydrocarbons	100 ppmv

Mostof the propane standards were NBS standards of propane in air.

Table C2-1 lists the data from 45 hydrocarbon standards analyses. The difference between the known and measured concentration and the percent difference is shown. The percent difference is defined as:

$$\% \text{ DIFF} = (\text{Known-Measured}) \times 100/\text{Known}.$$

Figures C2-1 and C2-2 contain plots of the difference and percent difference versus the measured concentration.

The differences ranged from - 88 ppm to + 66 ppm with an average difference of - 2.5 ppmv and a standard deviation of 22.5 ppm. A 95 percent confidence interval for the mean difference is - 2.5 ± 6.6 ppm, or - 9.1 to 4.1 ppm.

The percent differences ranged from - 54.6 to 12.9 percent with an average difference of - 1.65 percent and standard deviation of 9.9 percent. This gives a 95 percent confidence interval for the mean difference of - 1.65 ± 3.0 present, or - 4.7 to 1.4 percent.

2.1.1 Peak Height Versus Peak Area THC Quantification

Quantification of nonmethane hydrocarbons using the Byron THC for the first six refineries (A-F) in this program was based on the strip chart peak height. The analysis of standards beginning in Refinery "F" indicated some problems when quantifying gas mixtures using peak height. At Refinery "F," modifications to the THC analysis made it possible to determine nonmethane concentrations based on peak areas.

TABLE C2-1. HYDROCARBON BLIND STANDARDS ANALYSIS

	Hydrocarbon Concentration, ppmv			
Gas Type	Known Concentration	Measured Concentration[1]	Difference	Percent Difference
Propane	16.3	25.2	- 8.9	- 54.601
NBS[2] Propane	433.0	521.0	- 88.0	- 20.323
NBS Propane	147.0	161.0	- 14.0	- 9.524
NBS Propane	147.0	160.0	- 13.0	- 8.844
NBS Propane	722.0	770.0	- 48.0	- 6.648
NBS Propane	147.0	155.0	- 8.0	- 5.442
NBS Propane	147.0	155.0	- 8.0	- 5.442
NBS Propane	475.0	498.0	- 23.0	- 4.842
NBS Propane	147.0	154.0	- 7.0	- 4.762
NBS Propane	475.0	494.0	- 19.0	- 4.000
NBS Propane	147.0	152.0	- 5.0	- 3.401
NBS Propane	722.0	746.0	- 24.0	- 3.324
NBS Propane	722.0	744.0	- 22.0	- 3.047
NBS Propane	722.0	740.0	- 18.0	- 2.493
Propane	227.0	232.0	- 5.0	- 2.203
NBS Propane	147.0	150.0	- 3.0	- 2.041
NBS Propane	148.0	151.0	- 3.0	- 2.027
NBS Propane	722.0	734.0	- 12.0	- 1.662
NBS Propane	97.0	98.5	- 1.5	- 1.546
NBS Propane	97.0	98.5	- 1.5	- 1.546
NBS Propane	722.0	732.0	- 10.0	- 1.385
NBS Propane	147.0	149.0	- 2.0	- 1.361
NBS Propane	147.0	149.0	- 2.0	- 1.361
NBS Propane	722.0	730.0	- 8.0	- 1.108
Propane	227.0	228.0	- 1.0	- 0.441
NBS Propane	475.0	477.0	- 2.0	- 0.421
NBS Propane	722.0	725.0	- 3.0	- 0.416

Continued

TABLE C2-1. (Continued)

Gas Type	Hydrocarbon Concentration, ppmv Known Concentration	Measured Concentration[1]	Difference	Percent Difference
Propane	16.3	16.3	0.0	0.000
NBS Propane	97.0	96.9	0.1	0.103
Propane	227.0	226.0	1.0	0.441
$C_1 - C_6$	100.0	98.8	1.2	1.200
$C_1 - C_6$	100.0	98.8	1.2	1.200
NBS Propane	147.0	145.0	2.0	1.361
Hexane	525.0	516.0	9.0	1.714
Propane	227.0	222.0	5.0	2.203
Propane	227.0	221.8	5.2	2.291
NBS Propane	103.0	99.8	3.2	3.107
Propane	576.0	554.0	22.0	3.819
Propane	151.0	144.0	7.0	4.636
NBS Propane	722.0	684.0	38.0	5.263
NBS Propane	721.0	680.0	41.0	5.6865
Propane	721.0	655.0	66.0	9.1540
Propane	227.0	200.0	27.0	11.8943
Propane	117.0	102.0	15.0	12.8205
	16.3	14.2	2.1	12.8834

[1] Based on peak area.

[2] NBS = National Bureau of Standards

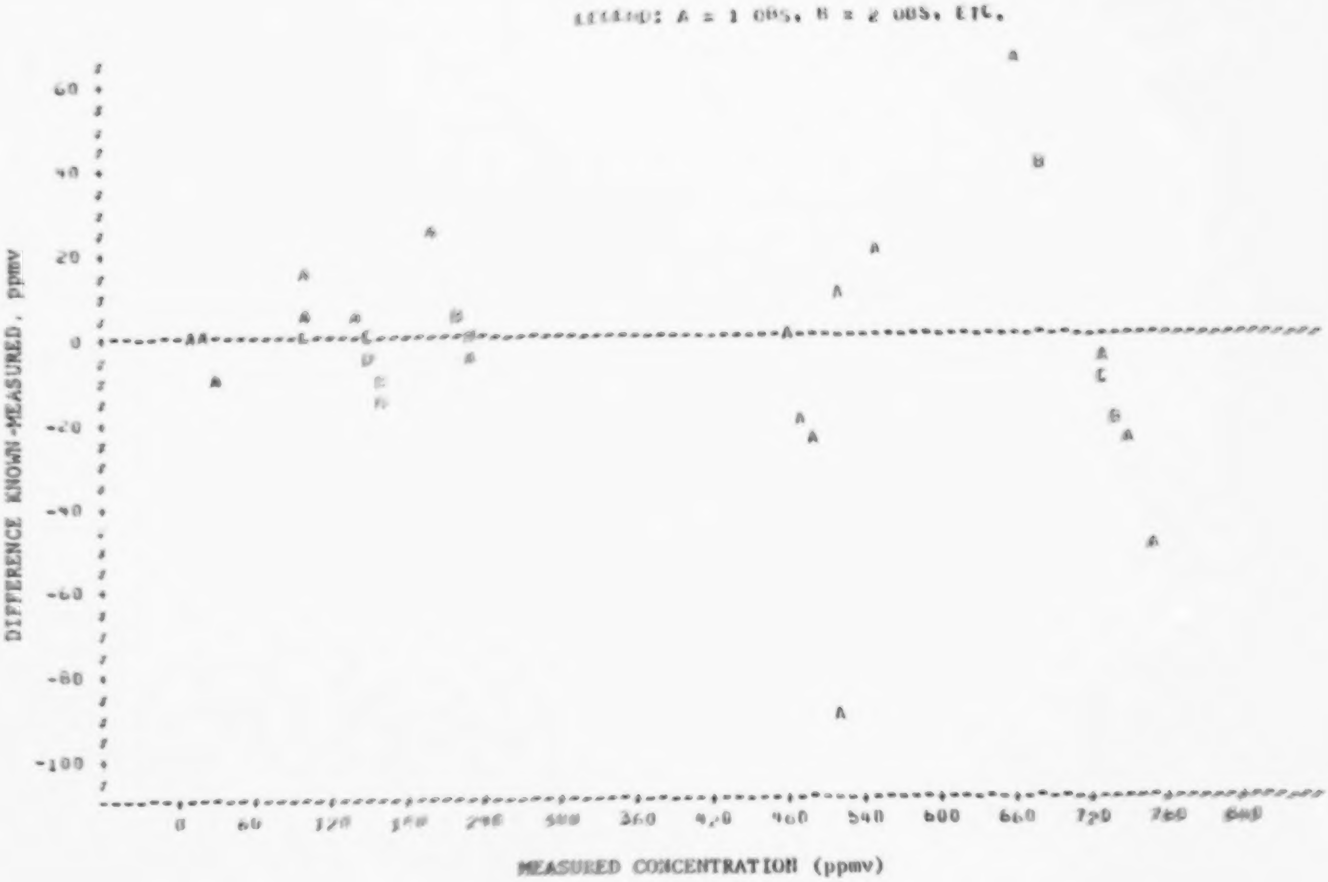

Figure C2-1. Hydrocarbon Blind Standards Analysis Differences

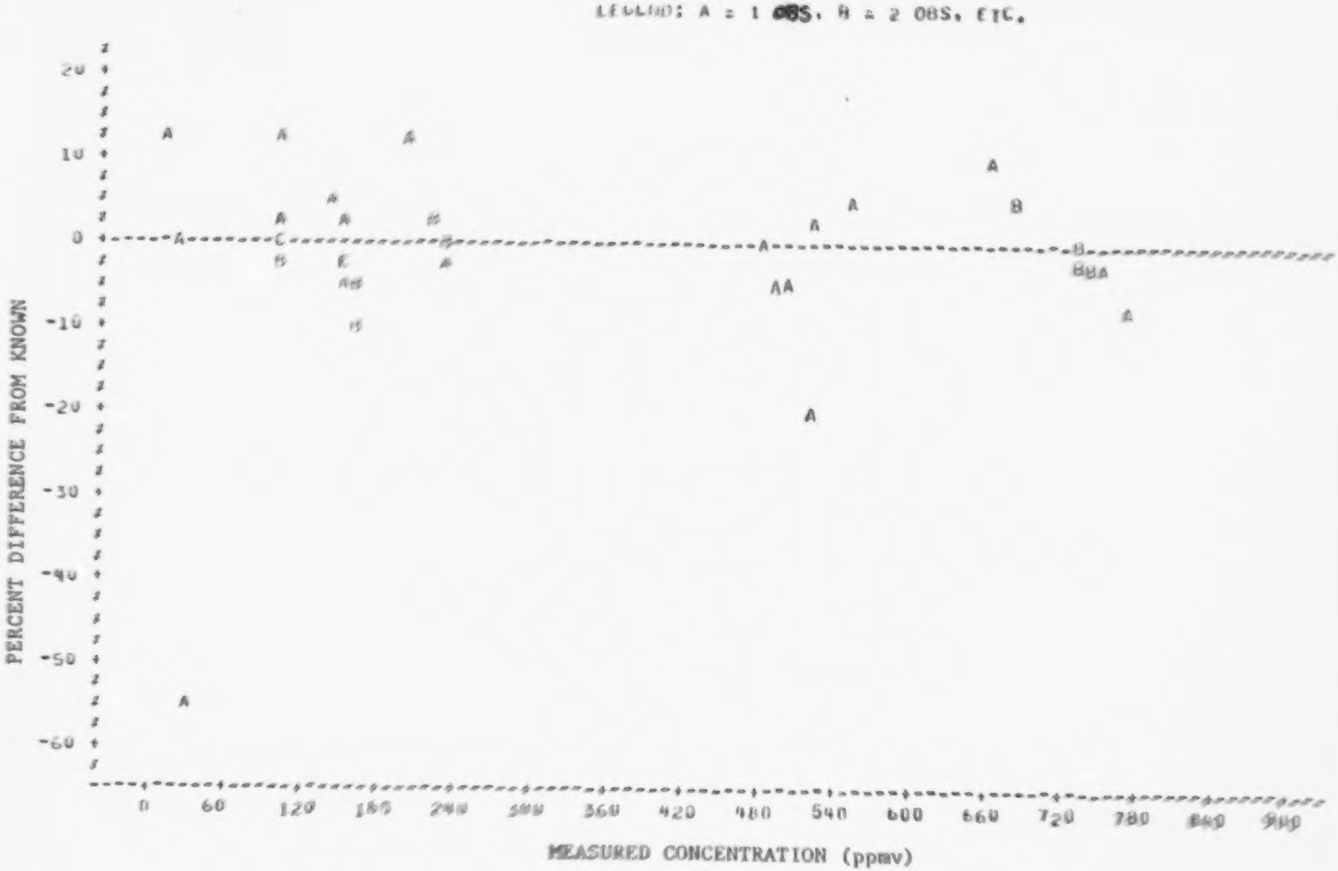

Figure C2-2. Hydrocarbon Blind Standards Analysis Percent Differences

Further research and standards analysis confirmed that more accurate concentrations are obtained using the peak area. In Refineries "G" through "I," the THC analyzer was calibrated based on peak height (as in previous refineries), but concentrations based on both peak height and peak area were recorded for all samples analyzed.

Further analyses of standard gas mixtures at Refineries "G" - "I" confirmed that concentrations based on peak height are usually biased high while concentrations based on peak area indicate no bias. The amount of bias in the peak height concentration depends on the particular mixtures of hydrocarbons being analyzed. The following table shows some results from different standards analyzed on the THC:

	Measured Concentration (ppm)		
Gas Standard	Peak Height	Peak Area	PH/PA Ratio
NBS - 147 ppm Propane	174.2	150	1.16
NBS - 722 ppm Propane	838	725	1.16
1616 ppm Hexane	2852	1680	1.70
2641 ppm Isopentane	5970	2700	2.21
1036 ppm $C_2 - C_6$	1760	1090	1.61

Data collected at Refineries "J" - "M" were quantified using peak areas with calibration also based on peak area. These data based on peak area were available for all refineries after Refinery "F."

The paired peak height and peak area (PH/PA) data from Refineries "G," "H," and "I" were analyzed in order to obtain adjustment factors to apply to the Refinery "A" - "F" data. Figure C2-3 graphically summarizes the data available for determining these factors. The diagonal line on the graph represents equality between the peak height and peak area determinations. A total of 399 pairs of PH/PA nonmethane readings (ppm) were available with an average PH/PA ratio of 1.30. Assuming the peak area measurement to be correct, then the peak height readings averaged about 30 percent higher.

Figure C2-4 shows the PH/PA ratio plotted against the total leak rate (lbs/hr) respectively. The dashed line on this plot represents a ratio of 1.0, or perfect agreement. The plot indicates a dependency of the ratio on the level of nonmethane hydrocarbon in the sample. The ratios for the very low concentrations appear closer to 1.0 than the higher concentrations. The higher concentrations will of course be most affected by a ratio or percentage adjustment. If only samples with concentrations greater than 10,000 ppm (based on peak height) are considered, there are 178 pairs with an average PH/PA ratio of 1.38. The ratios for these high concentrations range from 0.9 to 2.7.

Since the PH/PA ratio is highly dependent on the particular mixture of hydrocarbons in the sample, it would be desirable to know the exact proportion and types of hydrocarbons in the samples from Refineries "A" - "F" in order to make adjustments to the peak height concentrations. This information is not available, but the nearest thing to it in the refinery data base was the process stream codes. Table C2-2 lists the various codes with a summary of the PH/PA ratio information available for each code. Note that there are significant differences between the stream types, and that the ratio is quite variable within any particular type.

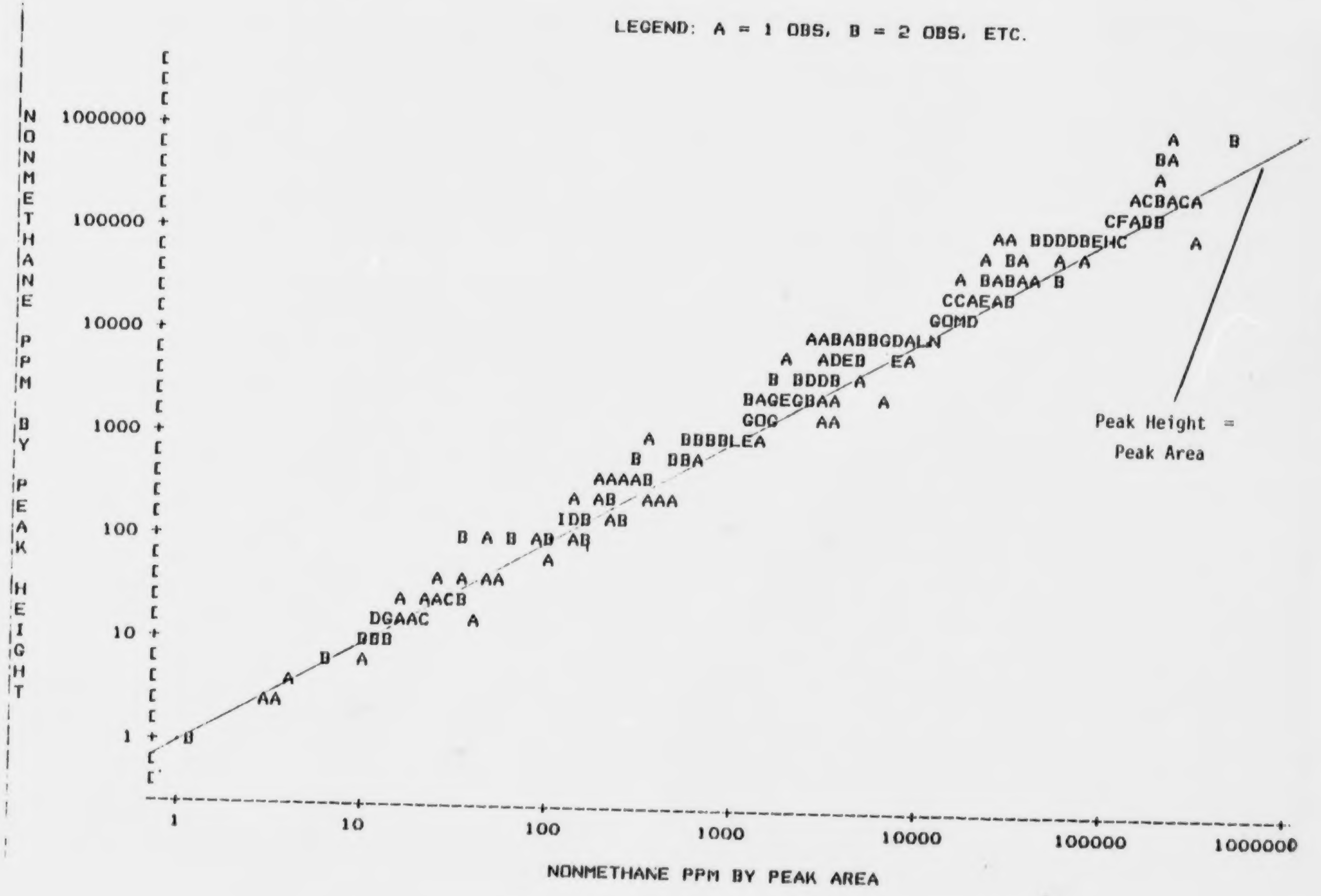

Figure C2-3. Evaluation of Peak Height Versus Area Determinations for Hydrocarbon

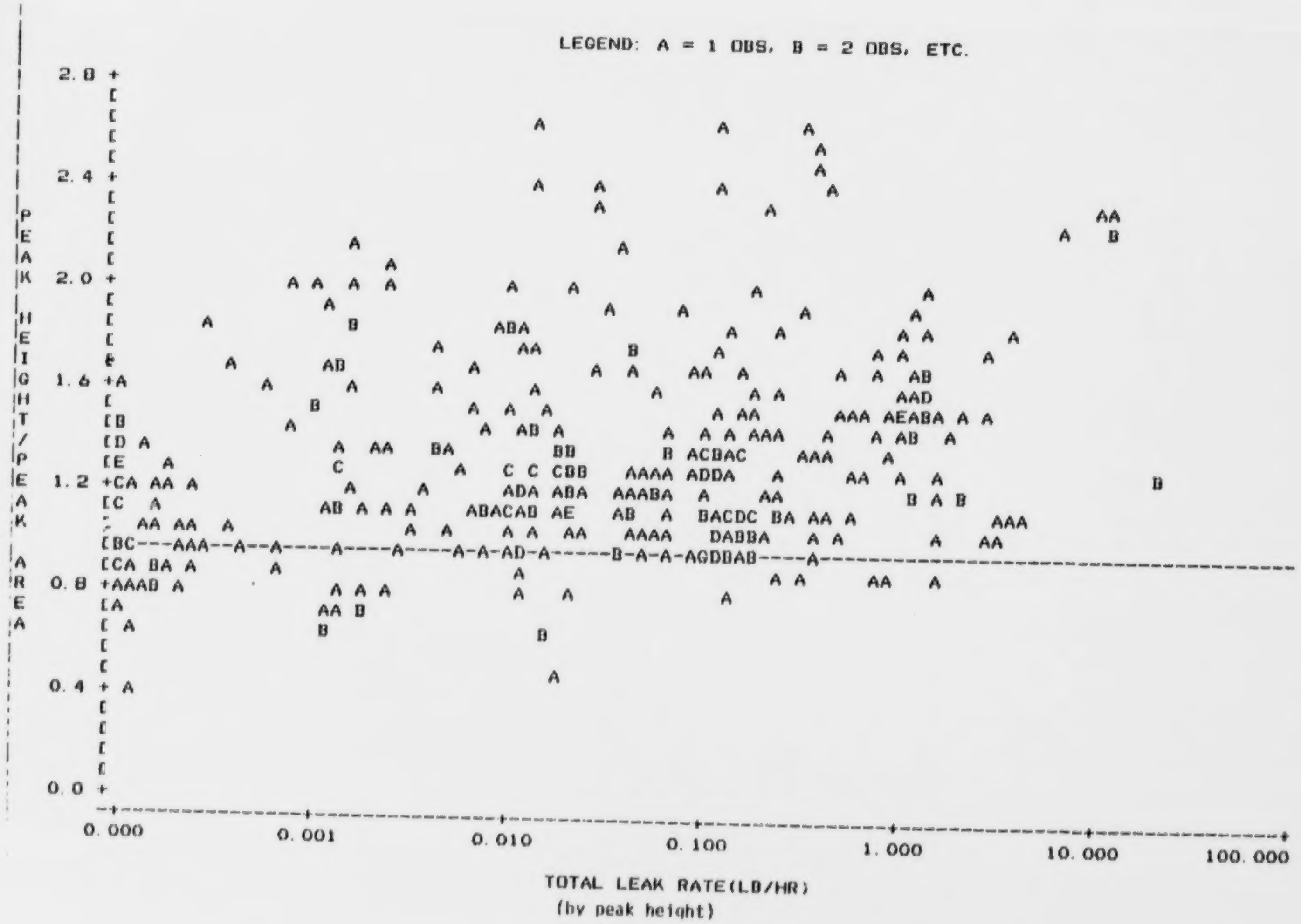

Figure C2-4. Peak Height to Area Ratio for Hydrocarbon Versus Leak Rate

TABLE C2-2. SUMMARY OF PH/PA[1] DATA FROM REFINERIES G - I BY PROCESS STREAM CODE

		ALL DATA				ONLY DATA WITH ppm > 10,000				
Process Stream Code	Process Stream Description	Number of Pairs of PH/PA	Average Ratio PH/PA	Low Ratio PH/PA	High Ratio PH/PA	Number of Pairs of PH/PA	Average Ratio PH/PA	Low Ratio PH/PA	High Ratio PH/PA	Adjustment Factor Used
--	Missing	23	1.23 ± 0.06	0.90	1.43	14	1.21 ± 0.08	0.92	1.43	1.4
AAAX	G/V Hydrocarbon $C_1 - C_2$	93	1.39 ± 0.06	0.62	2.63	60	1.43 ± 0.05	1.08	1.95	1.4
AABX	G/V Hydrocarbon $C_3 - C_4$	55	1.32 ± 0.11	0.97	2.46	28	1.37 ± 0.20	0.97	2.46	1.4
AACX	G/V Hydrocarbon $C_5 - C_9$	4	1.54 ± 0.26	1.34	1.93	1	1.34 -	-	-	1.5
ABAB	G/V Hydrocarbon > 50%	34	1.48 ± 0.16	0.61	2.67	10	1.79 ± 0.30	1.25	2.67	1.4
BCAX	LE/GL Distillate $C_1 - C_2$	2	1.32 -	1.31	1.34	0	- -	-	-	1.3
BCBX	LE/GL Distillate $C_3 - C_4$	94	1.14 ± 0.05	0.78	2.39	32	1.16 ± 0.10	0.90	2.39	1.2
BCCX	LE/GL Distillate $C_5 - C_8$	28	1.57 ± 0.17	0.84	2.60	9	1.77 ± 0.34	1.19	2.60	1.7
BCEX	LE/GL Distillate Naphthas	45	1.30 ± 0.17	0.46	2.43	15	1.40 ± 0.28	0.94	2.20	1.4
BCFX	Distillate Kerosene, etc.	4	0.86 ± 0.15	0.66	0.99	0	- -	-	-	1.1
BCGX	Distillate - Gas oils	11	1.20 ± 0.20	0.80	1.70	5	1.47 ± 0.28	0.95	1.70	1.1
BCHX	Distillate - Fractionator Bottoms	1	0.39 -	-	-	0	- -	-	-	1.1
BDAX	Nondistillate - H_2O > 50%	1	0.93 -	-	-	0	- -	-	-	1.1
CBAB	Gas/Liq Non-HC Hydrogen > 50%	4	1.01 ± 0.20	0.92	1.09	4	1.01 ± 0.20	0.92	1.09	1.4
	TOTAL	399	1.30 0.04	0.46	2.67	178	1.38 0.06	0.92	2.67	
Other Streams:										
	AADX									1.5
	BCDX									1.6
	BCJA									1.4
	All other streams									1.4

---

[1] PH/PA = (nonmethane hydrocarbons by peak height, ppm)/(nonmethane hydrocarbons by peak area, ppm)

Based on this analysis, the adjustment factors shown in Table C2-2 were applied to the nonmethane reading for all samples from Refineries "A" - "F" to create an estimated nonmethane reading based on peak area. Leak rates were then recalculated for all sources using the nonmethane area. The actual nonmethane hydrocarbon concentration based on area was used for the leak rate for the Refinery "G" - "M" data.

2.2 Replicate THC Analyses

The analysis for methane and nonmethane hydrocarbon content of fugitive emission gas samples was accomplished using a specially designed Total Hydrocarbon Analyzer (THC) Model 301C made for Radian by Byron Instruments. Analysis of baggable samples of gas is accomplished by pumping gas out of the Mylar sampling bag into a gas sample loop using an integral pump in the THC analyzer. The instrument operates automatically after being connected to the bag. The results of the first run are discarded to avoid contamination occurring from sample retained from the previous analysis or from ambient air entering the system during sample changing. The results of this run may, however, be used to select the proper attenuation ranges for methane and nonmethane hydrocarbons. Two additional runs are made and the results recorded by a strip-chart recorder. The results are immediately entered in a laboratory notebook and on the appropriate data sheet.

To document the precision of this analysis, pairs of runs were selected at each refinery and statistically analyzed. The pairs of runs for nonmethane hydrocarbon concentrations were randomly selected from those available using the following stratification:

Concentration Range Nonmethane Hydrocarbon (ppm)	Number of Samples Per Refinery	Total Number of Samples
< 1,000	2	26
1,001 - 10,000	2	26
10,001 - 50,000	2	26
50,001 - 200,000	2	26
> 200,000	2	26
	TOTAL PAIRS	136

The percent difference for each pair was calculated using:

$$\% \text{ DIFF} = \frac{\text{(1st analysis - 2nd analysis)}}{\text{Average of two analyses}}$$

Figures C2-5 and C2-6 show a plot of these percent differences versus each refinery and versus the average value. As can be seen, most differences were within the target limits of ± 7 percent. The ± 7 percent target was based on laboratory studies using hydrocarbon standards. A frequency distribution of the percent differences is shown in Figure C2-7.

The standard deviation was computed for each pair of readings. These standard deviations are shown graphically in Figure C2-8. The following statistics summarize the duplicate THC analyses.

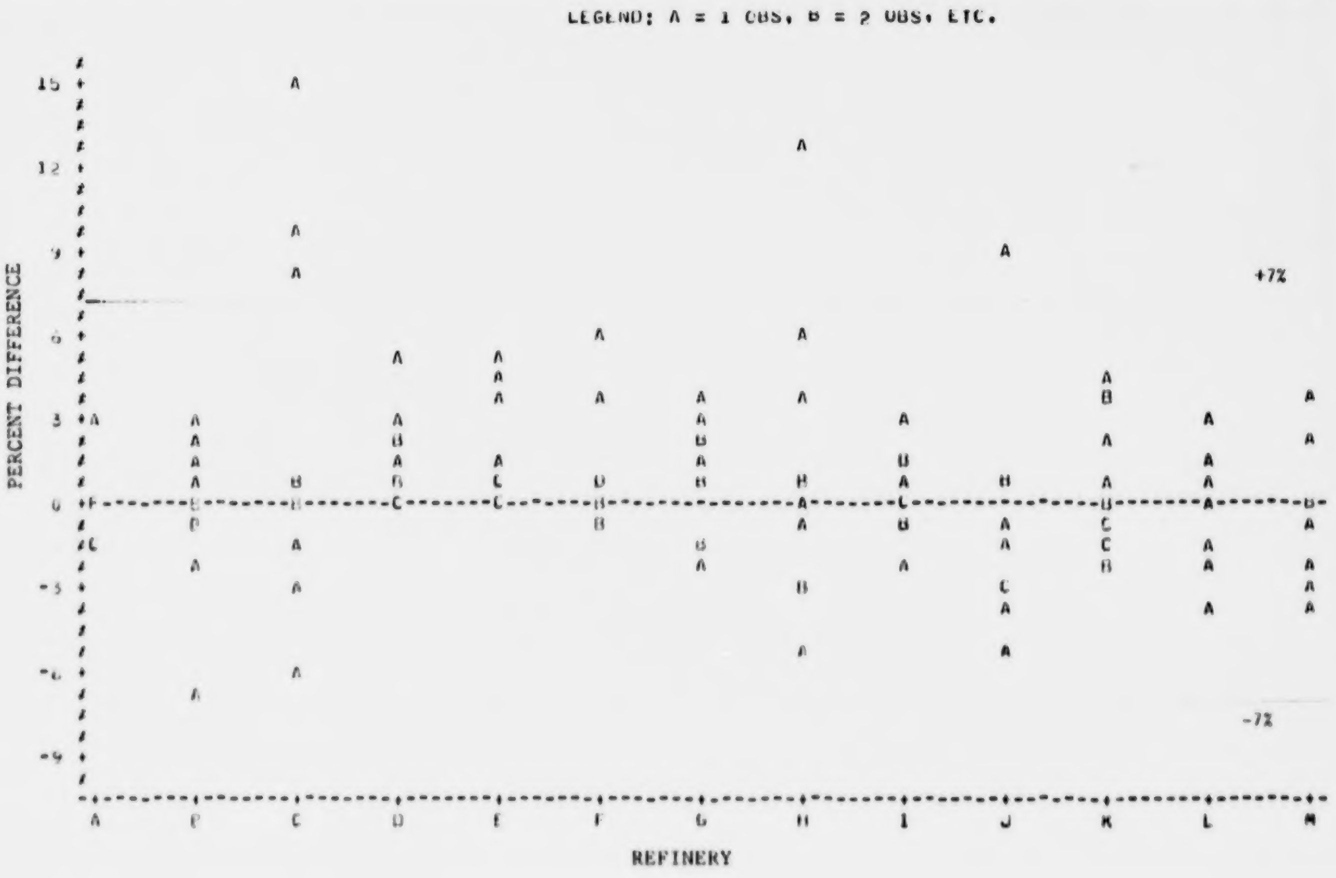

Figure C2-5. Percent Difference in Replicate THC Analysis for Each Refinery

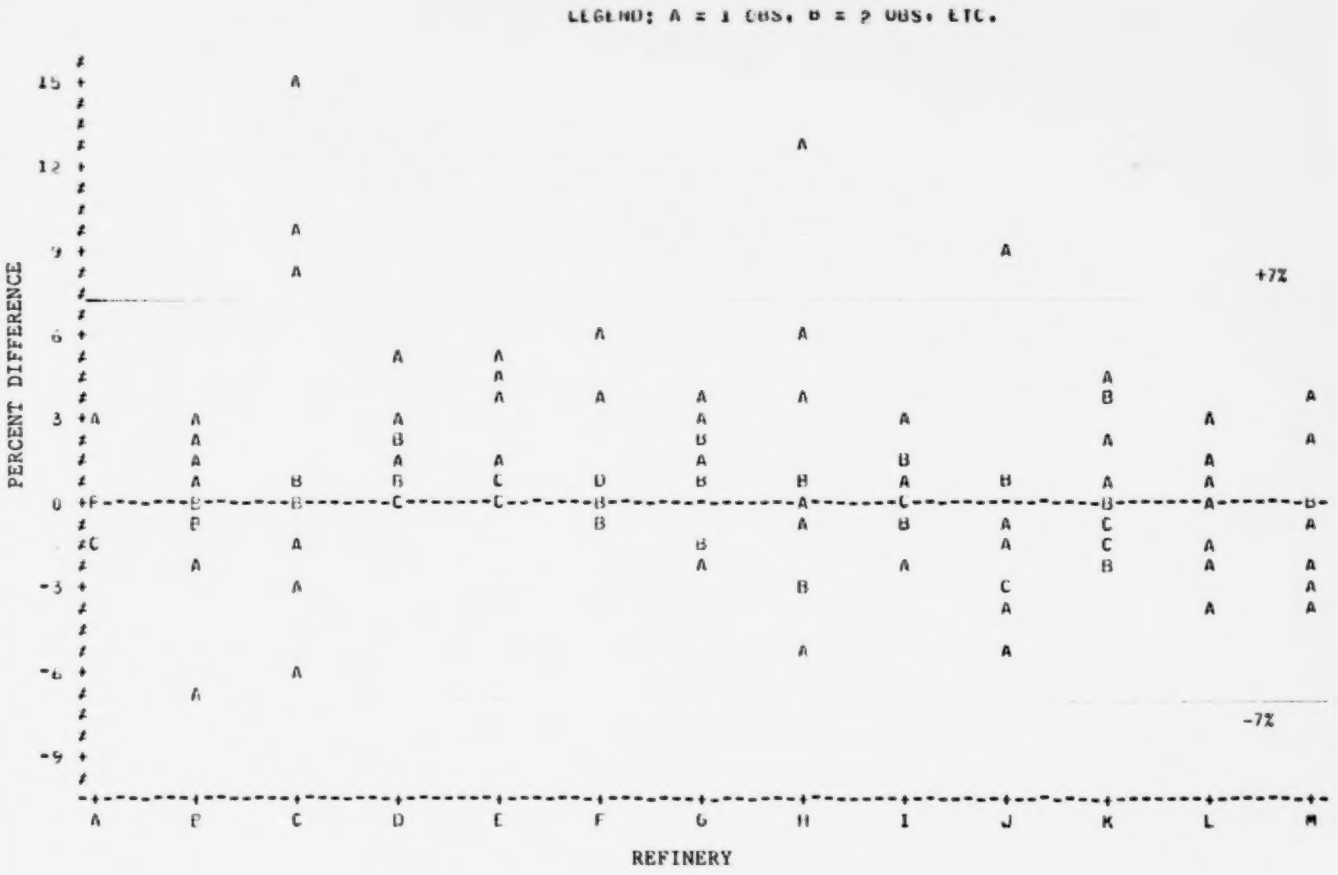

Figure C2-5. Percent Difference in Replicate THC Analysis for Each Refinery

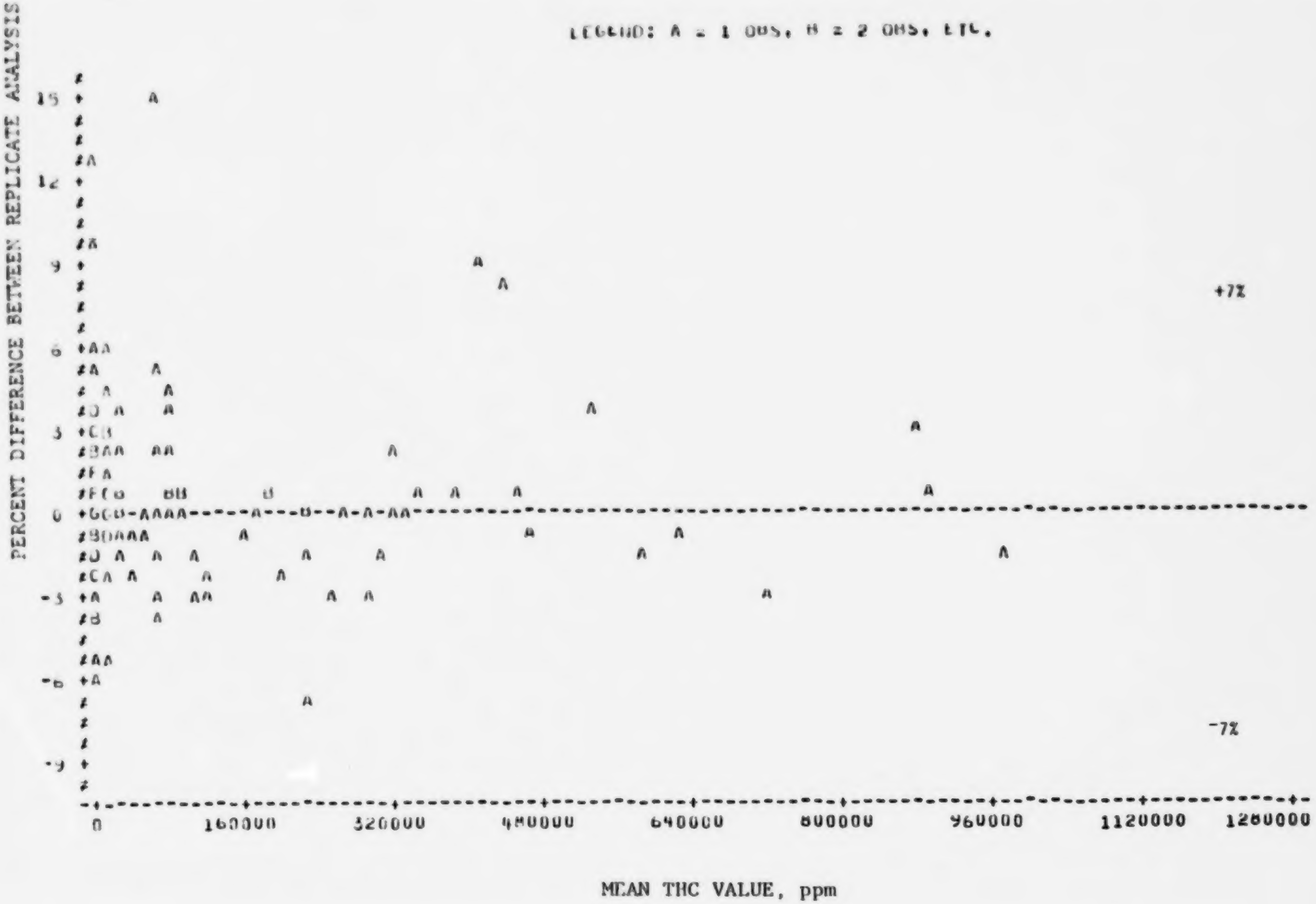

Figure C2-6. Percent Difference in Replicate THC Analysis Versus THC Level

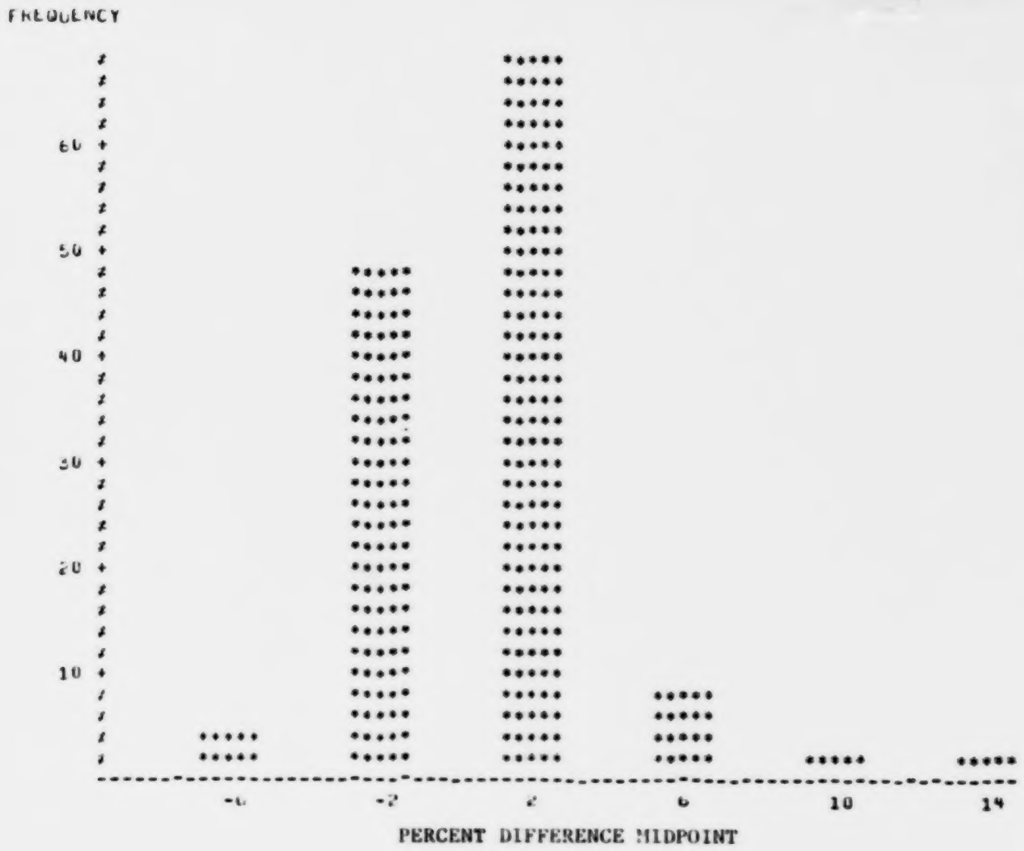

Figure C2-7. Frequency Bar Chart for Percent Differences in Replicate THC Analysis

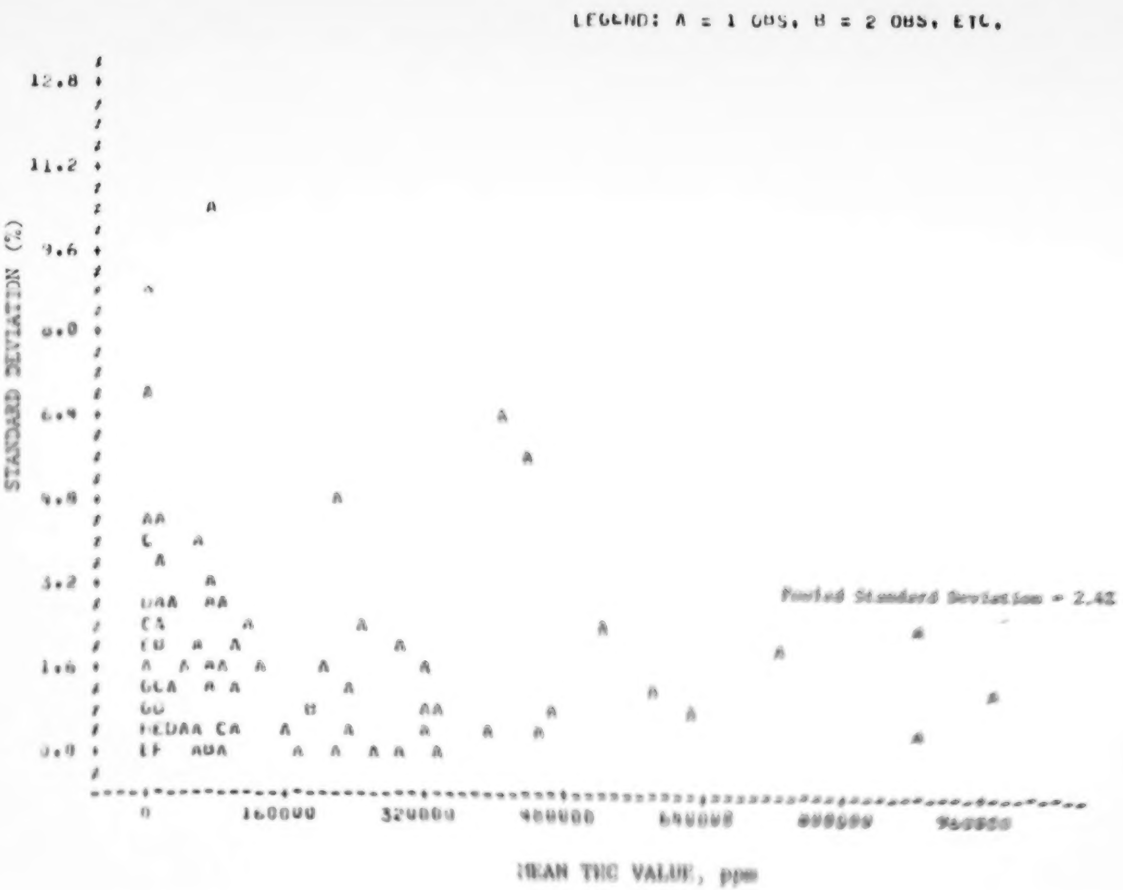

Figure C2-8. Standard Deviation for Replicate THC Analysis Versus THC Level

number of replicate pairs:	130
pooled standard deviation:	2.44%
repeatability - maximum difference expected between two readings 95 percent of time:	6.2%
95 percent confidence interval for mean reading based on single analysis:	± 4.8%
95 percent confidence interval for mean reading based on the average of two analyses:	± 3.4%

Since the average of the two readings was used in computing leaking for all sources, the ± 3.4 percent interval best describes the precision of the THC analysis.

2.3 Sampling and Analysis of Standards - Recovery Studies

To evaluate the overall accuracy of the baggable sampling and analysis technique, a procedure was devised to generate "known" leak rates. Standards of propane and propylene were used as the emissions source, and the leak rate was varied by altering the flow of these standards into the sampling cart. The use of flow meters to measure the rate of gas induced into the system introduced an additional source of variation into the sampling/analysis system. Extensive calibration procedures were followed to insure that no systematic error was introduced by using the flow meters. Samples of the induced leak were collected in bags (using the procedure described in Appendix A) and sent for THC analysis as a "blind standard."

Sixty-three recovery checks were made at the nine refineries visited beginning with Refinery "E." In addition, six similar checks were made of the sampling train by Research

Triangle Institute (RTI) during an EPA audit at Refinery "E." Eleven recovery checks were made at the Radian laboratory between the visits to Refineries "I" and "J." The induced leak rates ranged from 0.007 to 2.93 lbs/hr. Figure C2-9 shows a plot of the measured log leak rate versus the induced log leak rate. The slanted line on the plot represents 100 percent recovery of the induced leak rate. Figure C2-10 shows the percent recovery plotted versus the induced leak rate with the plotted symbol representing the refinery at which the check was made.

Figure C2-11 shows the recoveries obtained at each refinery in the order in which they were visited. The high recovery value of 235 percent obtained at Refinery "J" could not be explained for physical reasons. The value was eliminated from further statistical analysis after it was rejected using Dixon's statistical outlier test. The recovery values are shown for each refinery on a schematic plot in Figure C2-12. Some differences in average recovery rates are evident from these plots.

Table C2-3 contains a statistical summary of the recoveries at each refinery and overall. The results from the RTI audit are also given in the table. The 95 percent confidence intervals for the average recovery included 100 percent for all refineries except "F" and "G," with the upper limit for "G" at 98.5 percent. At Refinery "F" a new technique for pumping air through the sampling train was instituted. A check of the system after reviewing the accuracy checks showed that a low bias would be introduced by the way the pump was fitted. Therefore it was concluded that the leak rate data from Refinery "F" could be about 15 percent low. When the accuracy checks from Refinery "F" are removed, the remaining

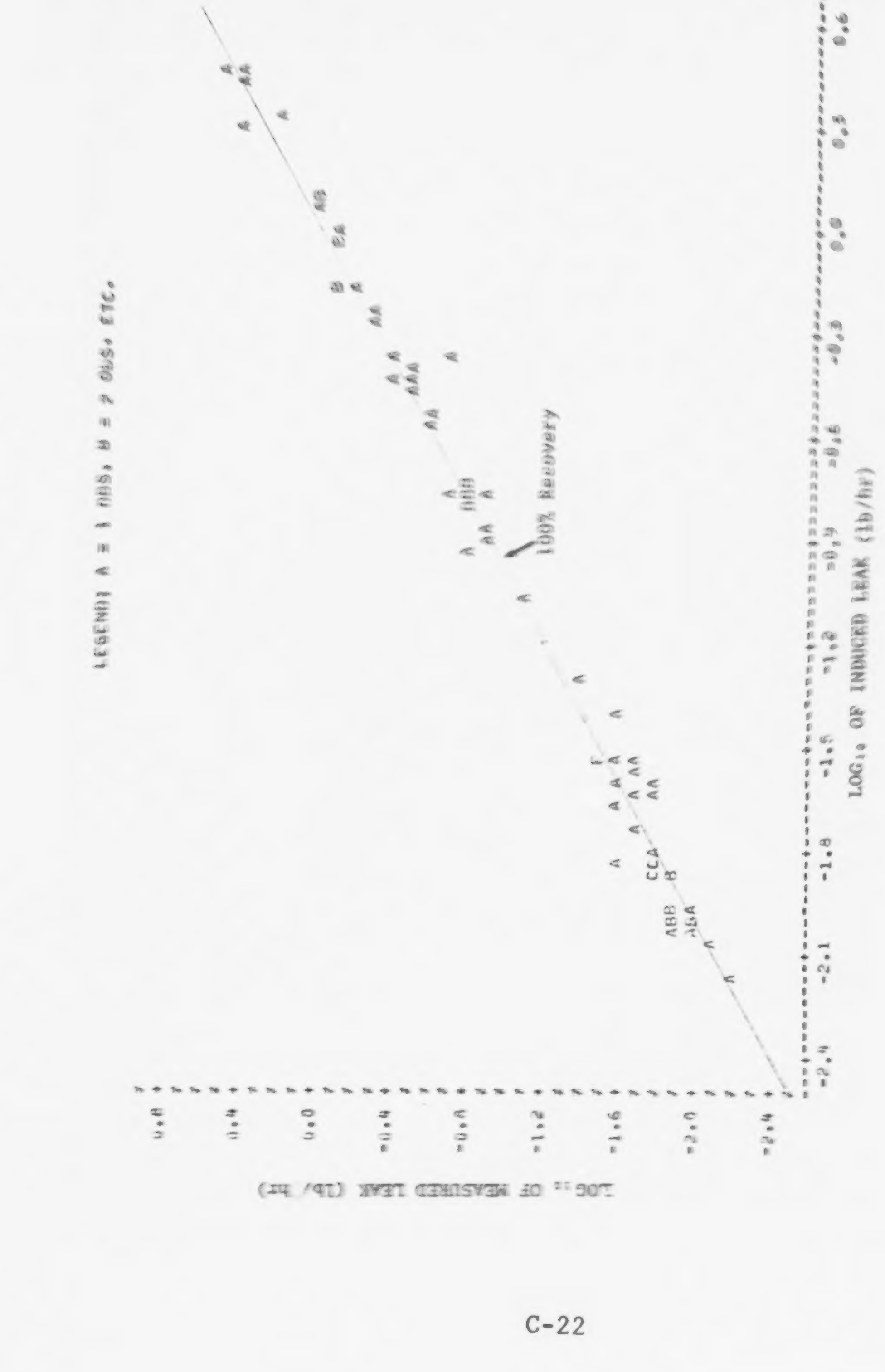

Figure C2-9. Recovery Studies - Measured Versus Induced Leak Rate

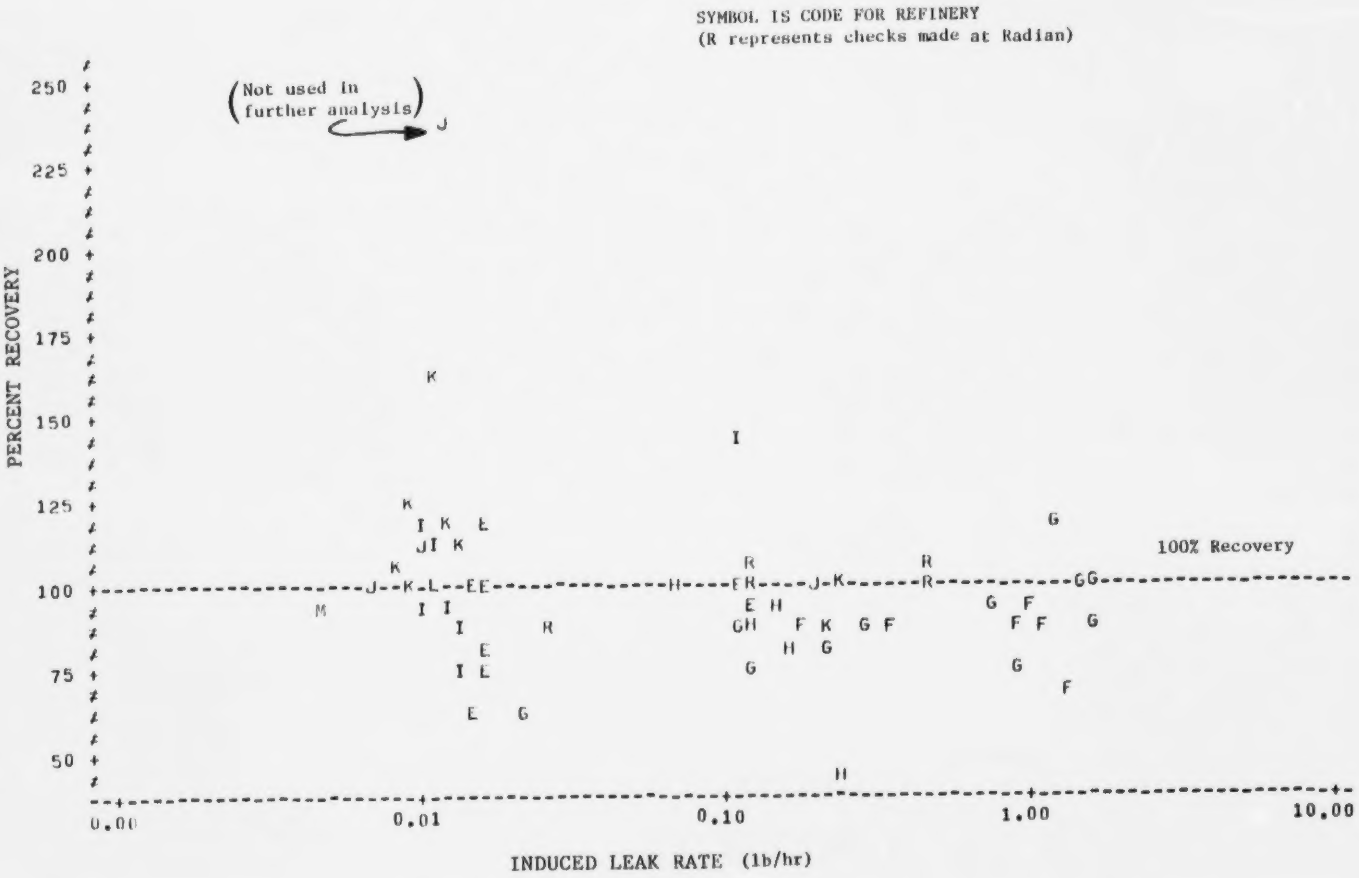

Figure C2-10. Recovery Studies - Percent Recovery Versus Induced Leak Rate

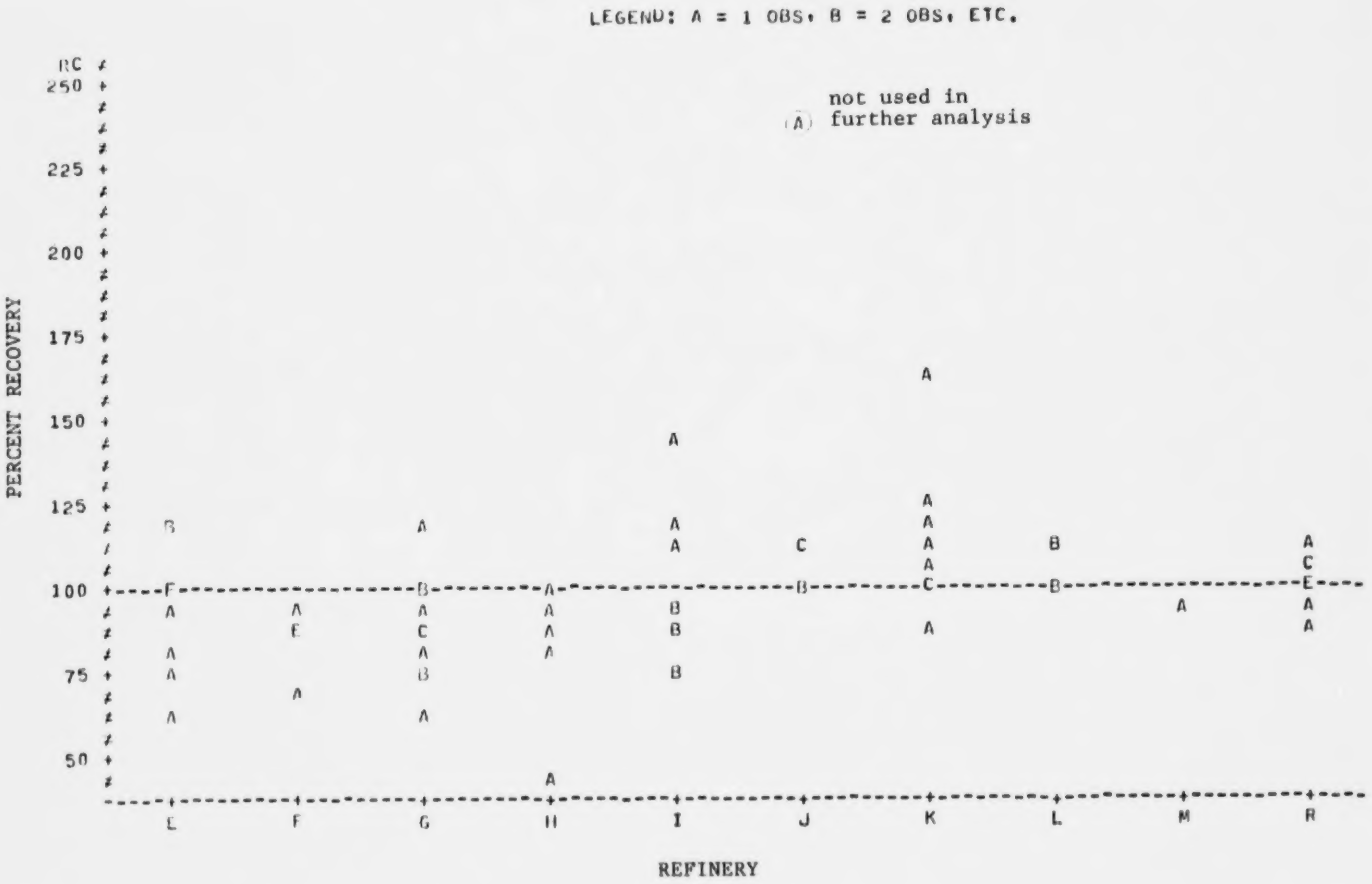

Figure C2-11. Recovery Studies - Percent Recovery Versus Refinery

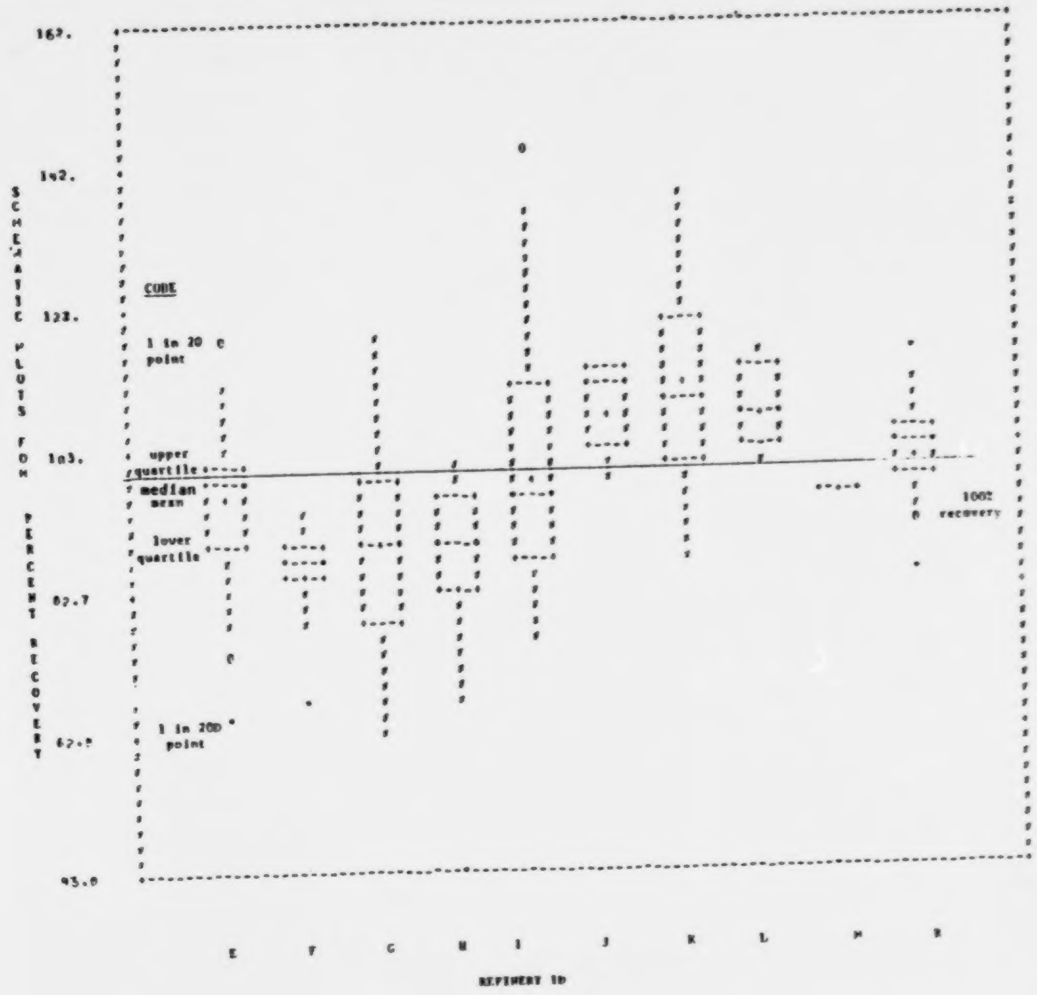

Figure C2-12. Sample Train Recovery Studies - Refinery Fugitive Emissions

TABLE C2-3. STATISTICAL SUMMARY OF RECOVERY STUDIES

REFINERY	NUMBER OF RECOVERY CHECKS	AVERAGE RECOVERY (%)	STANDARD DEVIATION OF RECOVERY (%)	RANGE OF RECOVERIES (%) MINIMUM	RANGE OF RECOVERIES (%) MAXIMUM	95% CONFIDENCE INTERVAL FOR AVERAGE RECOVERY (%)
E	12	95.3	15.5	64.4	118.8	(85.5 , 105.1)
F	7	85.7	8.5	66.9	92.8	(77.4 , 93.0)
G	11	89.0	14.2	63.5	117.6	(79.5 , 98.0)
H	5	82.4	22.5	44.0	100.0	(54.5 , 110.3)
I	9	99.2	22.0	76.0	145.0	(82.3 , 116.1)
J	5	107.4	7.1	97.4	113.6	(98.6 , 116.2)
K	9	112.3	21.2	88.0	161.3	(96.0 , 128.6)
L	4	107.4	7.0	100.7	115.3	(96.2 , 118.6)
M	1	96.5	--	--	--	-- --
Radian	11	100.7	7.5	85.6	114.8	(95.7 , 105.7)
TOTAL	74	97.4	17.2	44.0	161.3	(93.5 , 101.3)
TOTAL WITHOUT F	67	98.7	17.3	44.0	161.3	(94.5 , 102.9)
RTI AUDIT DURING REFINERY E	6	92.6	12.3	78.5	112.2	(79.7 , 105.5)

checks average 98.7 percent recovery with a 95 percent confidence interval of 95 to 103 percent. It was therefore concluded that there was no significant source of bias in the sampling/analysis system except for leak rate data from Refinery "F."

The amount of baggables data from Refinery "F" was as follows:

	Sources Screened at Refinery "F"		
Source Type	Number	% of the Total Sources Screened	Approximate Overall Bias (%)
Valves	268	12.1	- 1.8
Pump Seals	99	13.0	- 2.0
Flanges	98	4.8	- 0.7
Compressor Seals	5	2.2	- 0.3
Relief Valves	14	9.5	- 1.4
Drains	36	14.1	- 2.1
OVERALL	520	9.2%	- 1.4

If 9.2 percent of the data used in estimating emission factors were 15 percent low, then the emissions factors would be biased low by approximately 1.4 percent. Since this bias is relatively low, no attempt was made to adjust the actual leak rates obtained at Refinery "F." A systematic adjustment of the appropriate percent given above was made to each emission factor and confidence limit to eliminate this systematic bias. This adjustment is discussed in Section 6.3 of this appendix.

2.4 Repeated Samples from Individual Sources

A significant effort was extended throughout the field sampling program to evaluate the repeatability of the sampling/analysis procedures for baggable sources. Repeated samplings were done to determine the variability in the leak rate due to the sampling procedure, sampling teams, process changes, and level of leak rate. This determination was complicated by short-term variations in leak rates which were observed from individual sources. The number of quality control samples was as follows:

Source Type	Number of Sources Sampled	Number of Sources With QC Samples	Percent of Sources With QC Samples	Total Number of QC Samples
Valves	627	65	10.4	137
Pump Seals	382	62	16.2	133
Compressor Seals	124	40	32.3	66
Flanges	62	7	11.3	12
Relief Valves	52	16	30.7	30
Drains	49	14	28.6	33
TOTAL	1,296	204	15.7%	411

Approximately 16 percent of the sources sampled had one or more quality control samples with an average of about two quality control samples for each source with QC.

Initially one source for quality control was randomly selected in each of the following categories at each refinery:

Valves and Flanges	Intrateam reproducibility, Team 1, large fitting, high leak
	Interteam reproducibility, Team 1, large fitting, high leak
	Intrateam reproducibility, Team 2, large fitting, low leak
	Interteam reproducibility, Team 2, large fitting, low leak
	Intrateam reproducibility, Team 1, small fitting, low leak
	Interteam reproducibility, Team 1, small fitting, low leak
	Intrateam reproducibility, Team 2, small fitting, high leak
	Interteam reproducibility, Team 2, small fitting, high leak
Pumps	Intrateam reproducibility, Team 1, centrifugal, vapor leak
	Interteam reproducibility, Team 1, centrifugal, vapor leak
	Intrateam reproducibility, Team 2, centrifugal, vapor & liquid leak
	Interteam reproducibility, Team 2, centrifugal, vapor & liquid leak
	Intrateam reproducibility, Team 1, reciprocating, vapor & liquid leak
	Interteam reproducibility, Team 1, reciprocating, vapor & liquid leak
	Intrateam reproducibility, Team 2, reciprocating, vapor leak
	Interteam reproducibility, Team 2, reciprocating, vapor leak
Compressors	Intrateam reproducibility, Team 1, centrifugal
	Interteam reproducibility, Team 1, centrifugal
	Intrateam reproducibility, Team 2, reciprocating
	Interteam reproducibility, Team 2, reciprocating
Drains	Intrateam reproducibility, Team 1, homogeneous
	Interteam reproducibility, Team 1, homogeneous
	Intrateam reproducibility, Team 2, heterogeneous
	Interteam reproducibility, Team 2, heterogeneous
Relief Valves	Intrateam reproducibility, Team 1
	Interteam reproducibility, Team 1

This gave a total of about 26 quality control repeat samples for each refinery. Analysis of the baggables data after four refineries resulted in modified sampling and analysis procedures. Beginning with the fifth refinery, a revised procedure was used to select sources for quality control repeat samples. The following instructions were given:

> " (1) High Leakers (≥ 0.5 lbs/hr)
>
> For all samples with total leak rate greater than or equal to 0.5 lbs/hr, resample the source by two teams on different days. A data sheet is attached to record these special analyses. A regular data sheet should be prepared for each and noted "BQ" sample.

(2) Other Sources (0.01 lbs/hr < Leak Rate < 0.5 lbs/hr)

Select sources for QC checks at the following minimum rate per refinery:

• valves	3
• flanges	2
• pumps	2
• compressors	2
• drains	2
• relief valves	1

Resample the selected source by two teams. Have resampling done on the same day whenever possible.

If leaks > 0.01 lbs/hr are not found for a particular type of source, then ignore the requirement. If problems in the leak rate test procedure are detected, then additional QC checks should be made for the particular type of source indicating problems. "

Control charts were provided for recording the intra- and interteam differences at each refinery as soon as the analyses were completed. An example of the charts for one refinery are shown in Figure C2-13. This quality control selection procedure resulted in about 35 quality control baggables samples per refinery.

2.4.1 Results of Quality Control Samples

Table C2-4 contains the data for all of the repeat baggables samples. The first page of the table describes the codes used in the printout. For some sources with multiple samples, the individual percent differences for QC test results were not based on the original sample when it was obvious that the leak rate had changed by orders of magnitude since the time of the original sampling. Figures C2-14 through C2-19 show the percent differences for each QC check grouped by

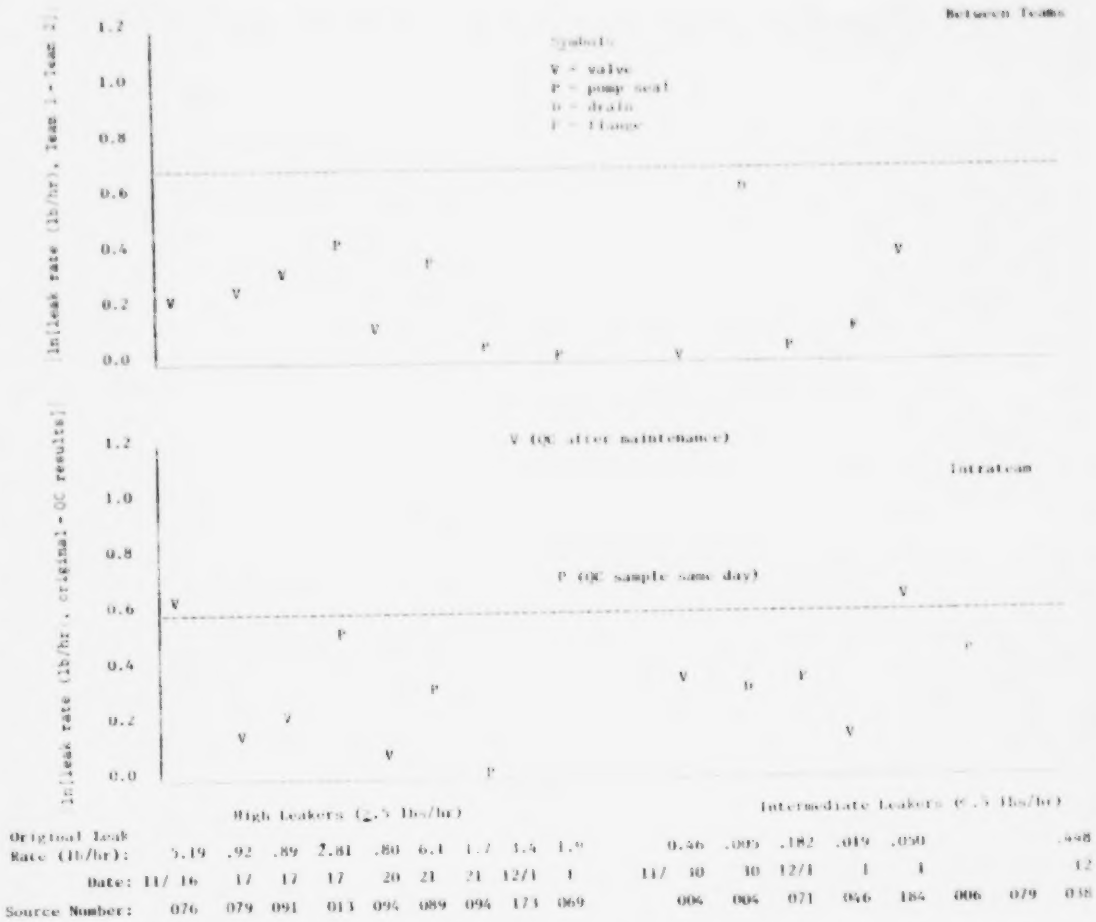

Figure C2-13. Example Quality Control Charts for Repeat Samples

TABLE C2-4. QUALITY CONTROL REPEAT SAMPLES[*]

CODE

(1) ID - Unit number/source type/ID number

(2) SAMP - BS - Original sample
BQ - Quality Control sample

(3) Date - Date of sampling

(4) Nonmethane Leak Rate - Leak rate (lbs/hr) of nonmethane hydrocarbons by THC

(5) INDIV % DIFF - $\frac{\text{original leak rate - QC leak rate}}{\text{(original + QC leak)/2}} \times 100$

(6) Mean NM Leak Rate - Average of original and QC leak rates for all samples for each ID

(7) Max % DIFF - Maximum percent difference between original and quality control samples where:

$$\text{\% DIFF} = \frac{\text{original leak rate - QC leak rate}}{\text{average of all leak rates}} \times 100$$

(8) Pooled Standard Deviation - Percent standard deviation of leak rates for each ID

$$- \left[\frac{\sum_{i=1}^{n} (\text{Individual \% Diff})^2}{2n} \right]^{1/2},$$

where n is the number of samples for the source.

---

[*] The QC data is sorted from low to high on Max % Diff.

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
27VA209	BS	50478	0.25254	.	0.25258	0.0	0.0
27VA209	BQ	50478	0.25261	-0.0			
1VA 97	BS	52577	0.00126	.	0.00126	0.5	0.3
1VA 97	BQ	52677	0.00126	-0.5			
2VA 6	BS	100477	0.00585	.	0.00587	0.7	0.4
2VA 6	BQ	100477	0.00589	-0.7			
13VA139	BS	52477	0.04814	.	0.04784	1.3	0.6
13VA139	BQ	52677	0.04753	1.3			
33VA 40	BS	51877	0.01768	.	0.01788	2.2	1.1
33VA 40	BQ	52777	0.01808	-2.2			
1VA 23	BS	30678	0.16038	.	0.16220	2.2	1.1
1VA 23	BQ	30778	0.16402	-2.2			
1VB 23	BS	30678	0.28208	.	0.28574	3.5	1.4
1VB 23	BQ	30678	0.29203	-3.5			
1VB 23	BQ	30678	0.28312	-0.4			
27VA211	BS	50478	0.38022	.	0.37583	3.5	1.4
27VA211	BQ	50478	0.38022	0.0			
27VA211	BQ	50478	0.36704	3.5			
5VA 52	BS	30378	0.23298	.	0.22685	5.4	2.7
5VA 52	BQ	30378	0.22072	5.4			
13VA 29	BS	40678	0.03219	.	0.03355	6.4	3.6
13VA 29	BQ	40778	0.03435	-6.5			
13VA 29	BQ	40678	0.03412	-5.8			
2VA 17	BS	100577	0.00810	.	0.00768	10.8	5.4
2VA 17	BQ	100577	0.00727	10.8			
3VA 83	BS	103078	0.01644	.	0.01741	11.2	5.6
3VA 83	BQ	110378	0.01838	-11.2			
13VA127	BS	52377	0.00323	.	0.00305	12.0	6.0
13VA127	BQ	52777	0.00286	12.0			
13VA134	BS	52477	0.00761	.	0.00712	13.7	6.9

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
13VA134	BQ	52677	0.00663	13.7			
13VA 94	BS	112077	0.69517	.	0.75087	14.7	6.8
13VA 94	BQ	112077	0.80541	-14.7			
13VA 94	BQ	112077	0.75202	-7.9			
8VA176	BS	50878	0.05108	.	0.05569	16.5	8.3
8VA176	BQ	50878	0.06029	-16.5			
34VA229	BS	82577	0.03132	.	0.03431	17.4	8.7
34VA229	BQ	82577	0.03731	-17.4			
15VA 11	BS	71377	0.00338	.	0.00373	17.8	8.2
15VA 11	BQ	71977	0.00362	-6.7			
15VA 11	BQ	71977	0.00387	-13.3			
15VA 11	BQ	71977	0.00405	-17.8			
27VA288	BS	32278	0.13622	.	0.12437	19.0	9.5
27VA288	BQ	32278	0.11253	19.0			
13VA144	BS	52377	0.00213	.	0.00240	22.6	11.3
13VA144	BQ	52677	0.00267	-22.6			
13VA259	BS	41278	0.07189	.	0.08289	26.6	13.3
13VA259	BQ	41278	0.09390	-26.6			
1VA 26	BS	12078	0.17606	.	0.16331	29.6	11.5
1VA 26	BQ	12378	0.18110	-2.8			
1VA 26	BQ	20778	0.13276	28.0			
15VA156	BS	20878	0.01538	.	0.01883	30.9	16.7
15VA156	BQ	21078	0.02119	-31.8			
15VA156	BQ	21078	0.01992	-25.7			
13VA140	BS	51277	0.11342	.	0.09779	32.0	16.0
13VA140	BQ	52777	0.08215	32.0			
2VA 67	BS	52377	0.02334	.	0.02000	33.4	16.7
2VA 67	BQ	52677	0.01666	33.4			
13VA118	BS	12578	0.01109	.	0.00935	35.5	16.2
13VA118	BQ	12678	0.00922	18.4			
13VA118	BQ	21078	0.00776	35.3			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS **VALVES**

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
36VA 4	BS	113077	0.02909	.	0.03745	36.2	20.5
36VA 4	BQ	113077	0.04061	-33.1			
36VA 4	BQ	113077	0.04264	-37.8			
15VA150	BS	20878	0.00171	.	0.00140	37.2	18.3
15VA150	BQ	20978	0.00131	26.5			
15VA150	BQ	20978	0.00119	36.0			
13VA117	BS	101977	0.21360	.	0.26540	39.0	19.5
13VA117	BQ	.	0.31720	-39.0			
27VA293	BS	32278	0.72107	.	0.78399	39.7	12.6
27VA293	BQ	32278	0.97118	-29.6			
27VA293	BQ	32278	0.65973	8.9			
2VA120	BS	90777	0.00142	.	0.00180	40.4	19.7
2VA120	BQ	90777	0.00184	-25.9			
2VA120	BQ	90777	0.00214	-40.8			
22VA 67	BS	70577	0.20311	.	0.17029	41.9	18.4
22VA 67	BQ	70577	0.17603	14.3			
22VA 67	BQ	70577	0.13172	42.6			
1VA150	BS	90777	0.06420	.	0.08442	43.1	22.2
1VA150	BQ	90777	0.08845	-31.8			
1VA150	BQ	90777	0.10060	-44.2			
13VA 79	BS	111777	0.65873	.	0.81395	44.3	18.6
13VA 79	BQ	112077	1.01912	-43.0			
13VA 79	BQ	111777	0.76401	-14.8			
1VA 33	BS	12078	0.16460	.	0.13158	45.4	21.2
1VA 33	BQ	12378	0.12525	27.2			
1VA 33	BQ	20778	0.10489	44.3			
13VA 91	BS	111777	0.77388	.	0.61355	53.3	23.6
13VA 91	BQ	112077	0.44711	53.5			
13VA 91	BQ	111777	0.61967	22.1			
13VA 76	BS	111677	2.93698	.	2.26410	55.4	25.3
13VA 76	BQ	111777	1.68367	54.2			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
13VA 76	BQ	111777	2.17166	30.0			
11VA145	BS	40778	0.00041	.	0.00032	56.1	24.6
11VA145	BQ	40778	0.00034	18.2			
11VA145	BQ	40778	0.00023	57.4			
13VA146	BS	31678	0.03607	.	0.05617	56.2	34.0
13VA146	BQ	32178	0.06479	-56.9			
13VA146	BQ	32178	0.06766	-60.9			
1VA 90	BS	102678	0.16392	.	0.12165	57.1	28.0
1VA 90	BQ	103078	0.10654	42.4			
1VA 90	BQ	110378	0.09447	53.8			
13VA 78	BS	111777	0.21049	.	0.21733	58.1	17.0
13VA 78	BQ	120777	0.25378	-18.6			
13VA 78	BQ	120777	0.25958	-20.9			
13VA 78	BQ	120777	0.13322	45.0			
13VA 78	BQ	120777	0.22956	-8.7			
22VA184	BS	120177	0.04769	.	0.03757	65.4	28.8
22VA184	BQ	120277	0.04187	13.0			
22VA184	BQ	120277	0.02313	69.3			
8VA181	BS	50878	0.00007	.	0.00005	72.2	36.1
8VA181	BQ	50878	0.00003	72.2			
22VA 95	BS	71977	0.00018	.	0.00012	73.5	36.2
22VA 95	BQ	70777	0.00009	66.9			
22VA 95	BQ	71977	0.00010	58.3			
4VA 70	BS	102678	0.00541	.	0.00390	77.8	38.9
4VA 70	BQ	103078	0.00238	77.8			
33VA 31	BS	51877	0.00458	.	0.00329	78.1	39.0
33VA 31	BQ	52677	0.00201	78.1			
13VA203	BS	11778	0.16407	.	0.10979	80.4	38.5
13VA203	BQ	12078	0.08950	58.8			
13VA203	BQ	20778	0.07579	73.6			
1VA 75	BS	102778	0.03813	.	0.02672	82.1	36.5

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
1VA 75	BQ	103078	0.01621	80.7			
1VA 75	BQ	110378	0.02582	38.5			
13VA 17	BS	50178	0.88769	.	0.69954	84.5	28.1
13VA 17	BQ	50978	0.56158	45.0			
13VA 17	BQ	50378	0.29676	99.8			
13VA 17	BQ	50978	0.61706	36.0			
13VA 17	BQ	50978	0.71980	20.9			
13VA 17	BQ	50978	0.77302	13.8			
13VA 17	BQ	50978	0.86500	2.6			
13VA 17	BQ	50978	0.75499	16.2			
13VA 17	BQ	50978	0.81993	7.9			
4VA 69	BS	102678	0.00269	.	0.00181	86.7	40.1
4VA 69	BQ	103078	0.00221	19.5			
4VA 69	BQ	110278	0.00112	82.3			
4VA 69	BQ	110378	0.00122	75.5			
13VA212	BS	11777	0.00183	.	0.00198	87.5	25.5
13VA212	BQ	12778	0.00119	42.5			
13VA212	BQ	20378	0.00292	-45.9			
1VA186	BS	72177	0.05349	.	0.07055	88.0	28.6
1VA186	BQ	71877	0.11013	-69.2			
1VA186	BQ	72177	0.04804	10.7			
27VA239	BS	103177	0.00496	.	0.00560	90.4	24.3
27VA239	BQ	103177	0.00352	33.8			
27VA239	BQ	103177	0.00387	24.6			
27VA239	BQ	103177	0.00451	9.4			
27VA239	BQ	103177	0.00814	-49.6			
27VA239	BQ	103177	0.00858	-53.5			
1VA 71	BS	102678	0.05137	.	0.02893	99.4	46.1
1VA 71	BQ	103078	0.02626	64.7			
1VA 71	BQ	103078	0.02260	77.8			
1VA 71	BQ	110278	0.02297	76.4			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
1VA 71	BQ	110378	0.02408	72.3			
1VA 71	BQ	110378	0.02633	64.5			
1VA 18	BS	100777	0.00452	.	0.00251	103.8	47.2
1VA 18	BQ	101277	0.00211	72.7			
1VA 18	BQ	101277	0.00227	66.1			
1VA 18	BQ	101277	0.00224	67.4			
1VA 18	BQ	101077	0.00200	77.4			
1VA 18	BQ	101077	0.00192	80.9			
13VA118	BS	101977	0.09135	.	0.19594	106.8	53.4
13VA118	BQ	101977	0.30052	-107			
5VA 53	BS	30378	0.40646	.	0.38085	110.8	38.9
5VA 53	BQ	32178	0.57895	-35.0			
5VA 53	BQ	30378	0.15713	88.5			
3VA 85	BS	102678	0.02929	.	0.07820	125.1	62.6
3VA 85	BQ	110378	0.12711	-125			
13VA 82	BS	112077	0.00818	.	0.00769	128.1	33.7
13VA 82	BQ	120777	0.00598	31.1			
13VA 82	BQ	120777	0.00594	31.7			
13VA 82	BQ	120777	0.01044	-24.3			
13VA 82	BQ	120777	0.00289	95.5			
13VA 82	BQ	120777	0.01275	-43.7			
1VA 77	BS	102778	0.00581	.	0.00309	136.3	62.7
1VA 77	BQ	103078	0.00160	113.6			
1VA 77	BQ	110378	0.00186	103.2			
13VA 94	BS	12478	0.62352	.	0.60563	167.1	72.2
13VA 94	BQ	12678	0.77769	-22.0			
13VA 94	BQ	12678	1.01679	-48.0			
13VA 94	BQ	20778	0.00450	197.1			
1VA 73	BS	102678	0.00628	.	0.00279	189.7	82.7
1VA 73	BQ	103078	0.00109	141.0			
1VA 73	BQ	110378	0.00099	145.4			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
13VA231	BS	11878	0.00587	.	0.01151	191.6	59.3
13VA231	BQ	12778	0.00234	85.9			
13VA231	BQ	13178	0.00517	12.9			
13VA231	BQ	20278	0.00434	30.0			
13VA231	BQ	20378	0.00627	-6.6			
13VA231	BQ	20678	0.01602	-92.7			
13VA231	BQ	20678	0.01426	-83.3			
13VA231	BQ	20678	0.02366	-120			
13VA231	BQ	20678	0.02237	-117			
13VA231	BQ	20678	0.02024	-110			
13VA231	BQ	20678	0.02244	-117			
13VA231	BQ	20678	0.00508	14.6			
13VA231	BQ	20678	0.00160	114.6			
13VA 32	BS	40678	0.01912	.	0.00960	198.3	99.2
13VA 32	BQ	41278	0.00008	198.3			
13VA263	BS	12778	0.00010	.	0.00086	261.6	76.2
13VA263	BQ	13078	0.00013	-31.6			
13VA263	BQ	20378	0.00235	-184			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
15PB 37	BS	20978	0.83631	.	0.84884	3.0	1.5
15PB 37	BQ	20978	0.86137	-3.0			
13PA 69	BS	31678	0.05187	.	0.05288	3.8	1.9
13PA 69	BQ	22478	0.05390	-3.8			
27PA 84	BS	32278	0.33109	.	0.34720	9.3	4.6
27PA 84	BQ	32278	0.36330	-9.3			
22PU 88	BS	51377	0.01169	.	0.01229	9.7	4.9
22PU 88	BQ	51377	0.01289	-9.7			
15PA 1	BS	22778	0.18363	.	0.19317	9.9	4.9
15PA 1	BQ	22878	0.20271	-9.9			
1PU 10	BS	100777	1.01889	.	1.09498	13.9	6.8
1PU 10	BQ	101277	1.02589	-0.7			
1PU 10	BG	101277	1.16410	-13.3			
1PU 10	BG	101277	1.17105	-13.9			
13PA 12	BS	40778	0.06513	.	0.06052	14.2	6.7
13PA 12	BQ	40778	0.05650	14.2			
13PA 12	BG	40778	0.05994	8.3			
5PA 38	BS	30278	0.11310	.	0.10502	15.4	7.7
5PA 36	BQ	30278	0.09693	15.4			
33PA 52	BS	51677	0.36832	.	0.34088	16.1	8.1
33PA 52	BQ	52777	0.31344	16.1			
15PA 44	BS	20878	0.33524	.	0.30890	17.1	8.5
15PA 44	BQ	21078	0.28257	17.1			
35PB 49	BS	91477	0.19288	.	0.21020	17.3	7.7
35PB 49	BQ	91477	0.22928	-17.2			
35PB 49	BQ	91477	0.20845	-7.8			
27PA 91	BS	13078	0.26599	.	0.24417	17.9	8.9
27PA 91	BQ	13178	0.22235	17.9			
27PA 79	BS	32278	0.57635	.	0.52434	19.8	9.9
27PA 79	BQ	32278	0.47233	19.8			
1PU 4	BS	100577	0.00051	.	0.00046	21.2	10.6

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
1PU 4	BO	100577	0.00041	21.2			
15PU 28	BS	41877	0.02364	.	0.02552	21.6	8.2
15PU 28	BQ	77	0.02290	3.2			
15PU 28	BQ	77	0.02713	-13.7			
15PU 28	BQ	52477	0.02842	-18.3			
27PA 47	BS	50478	1.47152	.	1.31946	23.0	11.5
27PA 47	BQ	50478	1.16740	23.0			
1PU 6	BS	100477	0.02687	.	0.02394	24.6	12.3
1PU 6	BQ	100477	0.02100	24.6			
13PB 15	BS	50978	0.04989	.	0.04519	25.5	10.9
13PB 15	BQ	50178	0.03836	26.1			
13PB 15	BQ	50978	0.04733	5.2			
13PA 11	BS	40678	2.32803	.	2.78227	27.5	14.8
13PA 11	BQ	40678	3.09342	-28.2			
13PA 11	BQ	40678	2.92536	-22.7			
33PU 55	BS	51777	0.03536	.	0.03067	30.6	15.3
33PU 55	BC	52677	0.02598	30.6			
15PA 15	BS	22878	0.46901	.	0.40534	31.4	15.7
15PA 15	BQ	22878	0.34166	31.4			
13PA 75	BS	12078	0.00428	.	0.00380	32.6	14.1
13PA 75	BQ	12778	0.00303	34.1			
13PA 75	BQ	20378	0.00409	4.5			
34PB 57	BS	82477	0.04019	.	0.03449	33.1	16.5
34PB 57	BQ	82477	0.02878	33.1			
22PA 71	BS	120177	0.13294	.	0.10712	36.2	19.7
22PA 71	BQ	120177	0.09203	36.4			
22PA 71	BQ	120177	0.09640	31.9			
27PA 90	BS	13078	2.10445	.	2.71112	41.1	20.7
27PA 90	BQ	13179	2.80951	-28.7			
27PA 90	BQ	13178	3.21941	-41.9			
15PA 38	BS	121277	0.34949	.	0.39939	43.2	15.4

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
15PA 38	BQ	121277	0.51068	-37.5			
15PA 38	BQ	121277	0.33798	3.3			
13PA 25	BS	50978	0.00202	.	0.00189	43.5	15.1
13PA 25	BQ	50178	0.00141	35.7			
13PA 25	BQ	50978	0.00223	-9.7			
1PU 11	BS	101077	0.00996	.	0.00826	44.0	17.8
1PU 11	BQ	101077	0.00932	6.6			
1PU 11	BQ	101177	0.00791	23.0			
1PU 11	BQ	101177	0.00776	24.9			
1PU 11	BQ	101177	0.00633	44.6			
27PA 94	BS	112177	1.46348	.	1.14468	45.2	22.7
27PA 94	BQ	112277	0.94574	43.0			
27PA 94	BQ	112177	1.02483	35.3			
33PB 52	BS	51877	0.08746	.	0.07120	45.7	22.8
33PB 52	BQ	52777	0.05494	45.7			
15PU 34	BS	41977	0.02257	.	0.01943	45.9	18.1
15PU 34	BQ	41977	0.02326	-3.1			
15PU 34	BQ	41977	0.01753	25.1			
15PU 34	BQ	41977	0.01436	44.5			
33PA 51	BS	51877	0.28217	.	0.36855	46.9	23.4
33PA 51	BQ	52777	0.45493	-46.9			
13PA 13	BS	111777	2.33523	.	2.98596	52.4	21.4
13PA 13	BQ	112077	2.72200	-15.3			
13PA 13	BQ	111777	3.90064	-50.2			
33PU 69	BS	42677	0.01058	.	0.01451	54.2	27.1
33PU 69	BQ	42277	0.01844	-54.2			
22PA 69	BS	120177	1.59632	.	2.49786	54.5	34.4
22PA 69	BQ	120177	2.95680	-59.8			
22PA 69	BQ	120177	2.94045	-59.3			
34PU 33	BS	92077	0.00845	.	0.01166	55.1	27.6
34PU 33	BQ	91777	0.01487	-55.1			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
15PA 6	BS	22778	0.15919	.	0.22606	59.2	29.6
15PA 6	BQ	22478	0.29293	-59.2			
13PA169	BS	12478	0.11830	.	0.18794	59.6	35.4
13PA169	BQ	12678	0.21527	-58.1			
13PA169	BQ	12678	0.23026	-64.2			
27PA 89	BS	112177	4.60925	.	6.54746	62.0	28.2
27PA 89	BQ	112177	8.67034	-61.2			
27PA 89	BQ	112177	6.36279	-32.0			
15PA100	BS	20978	0.00954	.	0.01445	64.9	32.3
15PA100	BQ	21078	0.01489	-43.8			
15PA100	BQ	21078	0.01891	-65.9			
13PA 6	BS	40678	0.26120	.	0.40164	69.9	35.0
13PA 6	BQ	40778	0.54208	-69.9			
15PB 1	BS	72077	0.00824	.	0.00932	70.0	19.0
15PB 1	BQ	72077	0.00726	12.7			
15PB 1	BQ	72077	0.01111	-29.7			
15PB 1	BQ	62677	0.00673	20.1			
15PB 1	BQ	72177	0.01325	-46.7			
27PA 85	BS	32278	0.49584	.	0.68563	71.2	27.6
27PA 85	BQ	32278	0.57730	-15.2			
27PA 85	BQ	32278	0.98376	-66.0			
17PU 12	BS	72577	0.11504	.	0.08424	73.1	36.6
17PU 12	BQ	72577	0.05344	73.1			
27PB 87	BS	13078	8.63776	.	13.99686	87.9	37.0
27PB 87	BQ	13078	12.41647	-35.9			
27PB 87	BQ	13078	20.93635	-83.2			
13PA 68	BS	11877	0.37719	.	0.25888	91.4	45.7
13PA 68	BQ	11978	0.14057	91.4			
1PA 66	BS	30778	0.00496	.	0.00324	96.5	43.0
1PA 66	BQ	30778	0.00294	51.2			
1PA 66	BQ	30778	0.00163	92.1			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
27PA 88	BS	32278	1.06046	.	1.78037	100.6	39.3
27PA 88	BQ	32278	1.42946	-29.6			
27PA 88	BQ	32278	2.85120	-91.6			
22PU 18	BS	70577	0.00594	.	0.00470	101.5	28.1
22PU 18	BQ	70577	0.00433	31.5			
22PU 18	BQ	70177	0.00368	47.1			
22PU 18	BQ	70577	0.00270	75.0			
22PU 18	BQ	70577	0.00551	7.6			
22PU 18	BQ	70577	0.00482	21.0			
22PU 18	BQ	70177	0.00314	61.8			
22PU 18	BQ	70177	0.00747	-22.8			
22PU 18	BQ	70177	0.00473	22.7			
15PA 16	BS	22878	0.22693	.	0.14683	109.1	54.6
15PA 16	BQ	22878	0.06673	109.1			
23PA 79	BS	120877	0.06506	.	0.18979	109.5	68.6
23PA 79	BQ	120977	0.20551	-104			
23PA 79	BQ	120977	0.19762	-101			
23PA 79	BQ	120977	0.20798	-105			
23PA 79	BQ	120777	0.27278	-123			
13PB 16	BS	50978	0.24441	.	0.29582	123.2	31.2
13PB 16	BQ	50178	0.14524	50.9			
13PB 16	BQ	50978	0.28380	-14.9			
13PB 16	BQ	50378	0.50984	-70.4			
13PA 76	BS	31678	0.00040	.	0.00025	125.1	62.6
13PA 76	BQ	31678	0.00009	125.1			
33PU 54	BS	51777	0.33828	.	0.91011	125.7	62.8
33PU 54	BQ	52777	1.48194	-126			
13PA148	BS	51177	0.33797	.	0.20483	130.0	65.0
13PA148	BQ	52777	0.07168	130.0			
13PA 92	BS	13078	0.00464	.	0.00266	133.2	52.5
13PA 92	BQ	20178	0.00375	21.2			

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TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
13PA 92	BQ	20178	0.00238	64.4			
13PA 92	BQ	20178	0.00430	7.6			
13PA 92	BQ	20278	0.00401	14.7			
13PA 92	BQ	20378	0.00243	62.5			
13PA 92	BQ	20778	0.00110	123.3			
13PA 92	BQ	20778	0.00159	97.7			
13PA 92	BQ	20778	0.00169	93.3			
13PA 92	BQ	20778	0.00139	107.8			
13PA 92	BQ	20778	0.00195	81.6			
15PU 30	BQ	51077	0.00123	180.2			
15PU 30	BQ	51077	0.00715	107.1			
15PU 30	BQ	51077	0.00528	151.3			
35PB 52	BS	91377	0.00531	.	0.19473	155.3	111
35PB 52	BQ	91377	0.27106	-192			
35PB 52	BQ	91377	0.30780	-193			
15PU 27	BS	41577	0.00900	.	0.03413	162.4	75.6
15PU 27	BQ	41577	0.00877	2.7			
15PU 27	BQ	41577	0.01461	-47.5			
15PU 27	BQ	41577	0.00964	-6.9			
15PU 27	BQ	41577	0.00851	5.7			
15PU 27	BQ	41577	0.01169	-26.0			
15PU 27	BQ	51077	0.06394	-151			
15PU 27	BQ	51077	0.03638	-121			
15PU 27	BQ	51077	0.04613	-135			
15PU 27	BQ	51077	0.05583	-144			
15PU 27	BQ	51077	0.05151	-140			
15PU 27	BQ	51077	0.05545	-144			
15PU 27	BQ	51077	0.05204	-141			
15PU 27	BQ	51077	0.05433	-143			
33PU 67	BS	42677	0.00400	.	0.02729	170.7	85.4
33PU 67	BQ	42977	0.05057	-171			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
PUMPS

ID		SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
1PA	1	BS	12377	5.74866	.	3.00031	183.2	91.6
1PA	1	BQ	12478	0.25197	183.2			
27PA	83	BS	13078	1.06161	.	0.44831	200.6	77.8
27PA	83	BQ	13177	0.26023	121.3			
27PA	83	BQ	13177	0.16234	146.9			
27PA	83	BQ	13178	0.30904	109.8			
27PA	89	BS	32278	0.64498	.	0.22520	279.8	110
27PA	89	BQ	32278	0.01497	190.9			
27PA	89	BQ	32278	0.01566	190.5			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
**COMPRESSORS

ID		SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
5CA	5	BS	41878	0.02627	.	0.02595	2.5	1.2
5CA	5	BQ	41878	0.02563	2.5			
1CA	12	BS	50878	0.93132	.	0.91059	4.6	2.3
1CA	12	BQ	50878	0.88986	4.6			
13CA	6	BS	32478	0.24676	.	0.25064	8.0	2.6
13CA	6	BQ	32478	0.26263	-6.2			
13CA	6	BQ	32478	0.24253	1.7			
13CD	5	BS	32078	19.96349	.	19.17267	8.2	4.1
13CD	5	BQ	32078	18.38186	8.2			
5CA	6	BS	41878	0.03930	.	0.03905	12.2	3.6
5CA	6	BQ	41878	0.04130	-5.0			
5CA	6	BQ	41878	0.03656	7.2			
33CA	3	BS	110778	0.36462	.	0.38915	12.6	6.3
33CA	3	BQ	110778	0.41369	-12.6			
33CB	3	BS	110778	0.36462	.	0.38915	12.6	6.3
33CB	3	BQ	110778	0.41369	-12.6			
13CA	1	BS	41278	0.18785	.	0.17496	13.7	6.5
13CA	1	BQ	41278	0.17320	8.1			
13CA	1	BQ	41278	0.16383	13.7			
32CA	4	BS	110778	0.03549	.	0.03272	16.9	8.5
32CA	4	BQ	110778	0.02995	16.9			
32CB	4	BS	110778	0.03549	.	0.03272	16.9	8.5
32CB	4	BQ	110778	0.02995	16.9			
32CC	4	BS	110778	0.03549	.	0.03272	16.9	8.5
32CC	4	BQ	110778	0.02995	16.9			
23CC	11	BS	42078	0.45097	.	0.41329	18.2	9.1
23CC	11	BQ	42078	0.37562	18.2			
23CA	10	BS	42078	0.51442	.	0.46652	20.5	10.3
23CA	10	BQ	42078	0.41863	20.5			
5CB	6	BS	41878	0.25757	.	0.29209	26.1	11.3
5CB	6	BQ	41878	0.33375	-25.8			
5CB	6	BQ	41878	0.28493	-10.1			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
**COMPRESSORS

ID		SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
5CA	7	BS	41878	0.04724	.	0.04348	33.1	12.9
5CA	7	BQ	41878	0.03441	31.4			
5CA	7	BG	41878	0.04879	-3.2			
5CB	7	BS	41978	0.07648	.	0.08675	34.9	13.5
5CB	7	BQ	41978	0.07702	-0.7			
5CB	7	BQ	41978	0.10674	-33.0			
1CO	10	BS	50878	0.02327	.	0.02099	39.4	15.9
1CO	10	BG	50978	0.02398	-3.0			
1CO	10	BQ	50978	0.01571	38.8			
13CB	1	BS	41278	1.62669	.	1.55667	42.6	13.7
13CB	1	BQ	41278	1.85333	-13.0			
13CB	1	BQ	41278	1.19000	31.0			
13CA	1	BS	110778	0.25191	.	0.33368	49.0	24.5
13CA	1	BQ	110778	0.41545	-49.0			
13CB	1	BS	110778	0.25191	.	0.33368	49.0	24.5
13CB	1	BQ	110778	0.41545	-49.0			
13CC	1	BS	110778	0.25191	.	0.33368	49.0	24.5
13CC	1	BQ	110778	0.41545	-49.0			
13CD	1	BS	110778	0.25191	.	0.33368	49.0	24.5
13CD	1	BQ	110778	0.41545	-49.0			
27CO	18	BS	102777	0.22207	.	0.20937	49.9	16.1
27CO	18	BQ	102877	0.24620	-10.3			
27CO	18	BQ	102877	0.22745	-2.4			
27CO	18	BQ	102877	0.14176	44.1			
1CO	13	BS	71877	0.00312	.	0.00305	49.9	15.2
1CO	13	BQ	71877	0.00378	-19.3			
1CO	13	BQ	71877	0.00226	31.9			
1CB	11	BS	50978	0.12169	.	0.11955	50.7	15.4
1CB	11	BQ	50878	0.14876	-20.0			
1CB	11	BQ	50978	0.08819	31.9			
22CO	7	BS	70777	0.23107	.	0.18165	54.4	27.2

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
**COMPRESSORS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
22CO 7	BQ	70877	0.13222	54.4			
13CB 3	BS	12578	0.71773	.	0.62284	59.2	23.0
13CB 3	BQ	12578	0.73619	-2.5			
13CB 3	BQ	12678	0.67015	6.9			
13CB 3	BQ	20978	0.36729	64.6			
13CC 1	BS	41278	0.42025	.	0.33989	62.3	27.7
13CC 1	BQ	41278	0.20856	67.3			
13CC 1	BQ	41278	0.39087	7.2			
13CA 7	BS	32478	0.60471	.	0.44437	64.4	29.8
13CA 7	BQ	32478	0.31848	62.0			
13CA 7	BQ	32478	0.40992	38.4			
23CD 8	BS	41978	0.82955	.	0.59704	72.6	32.8
23CD 8	BQ	42078	0.56560	37.8			
23CD 8	BQ	42078	0.39598	70.8			
22CB 1	BS	111578	0.54721	.	1.19329	108.3	54.2
22CB 1	BQ	111578	1.83938	-108			
13CA 3	BS	12578	0.00571	.	0.01512	109.7	63.6
13CA 3	BQ	12678	0.01735	-101			
13CA 3	BQ	12678	0.02230	-118			
23CC 9	BS	42078	5.79976	.	3.43370	112.4	51.6
23CC 9	BQ	42078	2.56271	77.4			
23CC 9	BQ	42078	1.93861	99.8			
23CC 10	BS	42078	1.08153	.	0.87025	147.1	65.6
23CC 10	BQ	42078	1.40449	-26.0			
23CC 10	BQ	42078	0.12472	158.6			
22CO 9	BS	71877	1.42347	.	1.83031	150.0	49.3
22CO 9	BQ	70877	0.43165	106.9			
22CO 9	BQ	70877	3.17714	-76.2			
22CO 9	BQ	70877	2.28897	-46.6			
8CA 2	BS	110778	0.00034	.	0.00167	159.3	79.7
8CA 2	BQ	110778	0.00300	-159			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
**COMPRESSORS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
8CB 2	BS	110778	0.00034	.	0.00167	159.3	79.7
8CB 2	BQ	110778	0.00300	-159			
8CC 2	BS	110778	0.00034	.	0.00167	159.3	79.7
8CC 2	BQ	110778	0.00300	-159			
23CO 6	BS	120877	0.01684	.	0.04203	166.1	64.6
23CO 6	BQ	120877	0.04629	-93.3			
23CO 6	BQ	120877	0.06221	-115			
23CO 6	BQ	120777	0.07805	-129			
23CO 6	BQ	120777	0.00824	68.6			
23CO 6	BQ	120977	0.04059	-82.7			
34CO 5	BS	92077	0.00024	.	0.09111	199.5	99.8
34CO 5	BQ	92177	0.18198	-199			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
FLANGES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
1FL284	BS	90877	0.02520	.	0.02604	7.4	3.1
1FL284	BQ	90877	0.02712	-7.3			
1FL284	BQ	90877	0.02580	-2.3			
33FL 46	BS	120177	0.01247	.	0.01133	16.9	8.6
33FL 46	BQ	120177	0.01096	12.9			
33FL 46	BQ	120177	0.01055	16.7			
13FL 87	BS	11877	0.14735	.	0.18173	37.8	18.9
13FL 87	BQ	11978	0.21611	-37.8			
1FL 13	BS	12377	0.00128	.	0.00103	48.5	24.2
1FL 13	BQ	12378	0.00078	48.5			
13FL 57	BS	31678	0.00423	.	0.00673	60.3	35.5
13FL 57	BQ	32178	0.00829	-64.8			
13FL 57	BQ	32178	0.00767	-57.7			
1FL 4	BS	12078	0.10074	.	0.10403	60.8	17.7
1FL 4	BQ	12378	0.07405	30.5			
1FL 4	BQ	12478	0.13729	-30.7			
13FL 42	BS	12478	0.00967	.	0.00410	222.4	90.0
13FL 42	BQ	12678	0.00206	129.7			
13FL 42	BQ	12678	0.00056	178.2			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
RELIEF VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
27RV 17	BS	42878	0.28651	.	0.28854	1.4	0.7
27RV 17	BQ	42878	0.29058	-1.4			
13RV 43	BS	41378	0.17006	.	0.17137	1.5	0.8
13RV 43	BQ	41378	0.17269	-1.5			
13RV 38	BS	41378	0.24396	.	0.24090	2.5	1.3
13RV 38	BQ	41378	0.23784	2.5			
13RV 30	BS	41278	0.14552	.	0.14336	3.0	1.5
13RV 30	BQ	41278	0.14120	3.0			
13RV 2	BS	41178	0.00510	.	0.00495	5.9	3.0
13RV 2	BQ	41178	0.00481	5.9			
27RV 13	BS	50378	4.50774	.	4.71810	8.9	4.5
27RV 13	BQ	50378	4.92846	-8.9			
13RV 20	BS	50378	0.01046	.	0.01113	12.0	6.0
13RV 20	BQ	50378	0.01180	-12.0			
13RV 3	BS	41178	1.08040	.	0.97544	16.4	9.1
13RV 3	BQ	41178	0.92528	15.5			
13RV 3	BQ	41178	0.92064	16.0			
13RV 12	BS	12678	0.08214	.	0.08293	17.9	5.2
13RV 12	BQ	12678	0.09073	-9.9			
13RV 12	BQ	12678	0.07592	7.9			
23RV 28	BS	120877	2.52460	.	2.41117	26.0	8.1
23RV 28	BQ	120877	2.01772	22.3			
23RV 28	BQ	120877	2.45882	2.6			
23RV 28	BQ	120877	2.64355	-4.6			
13RV 49	BS	41378	0.15082	.	0.13271	27.3	13.6
13RV 49	BQ	41378	0.11461	27.3			
13RV 25	BS	11978	3.78514	.	3.32620	27.6	13.8
13RV 25	BQ	11978	2.86726	27.6			
13RV 1	BS	41178	0.02199	.	0.01756	44.4	21.1
13RV 1	BQ	41178	0.01419	43.1			
13RV 1	BQ	41178	0.01649	28.6			
13RV 29	BS	41278	0.06284	.	0.09764	58.7	33.9

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
RELIEF VALVES

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
13RV 29	BQ	41278	0.10991	-54.5			
13RV 29	BQ	41278	0.12016	-62.7			
27RV 3	BS	42778	2.52797	.	4.04323	70.2	35.3
27RV 3	BQ	42778	3.78700	-39.9			
27RV 3	BQ	42778	2.67706	-5.7			
27RV 3	BQ	42778	3.71492	-38.0			
27RV 3	BQ	42778	5.36545	-71.9			
27RV 3	BQ	42778	5.29777	-70.8			
27RV 3	BQ	42778	4.93244	-64.5			
27RV 4	BS	42778	0.24242	.	0.47288	115.1	51.4
27RV 4	BQ	42778	0.16687	36.9			
27RV 4	BQ	42778	0.59731	-84.5			
27RV 4	BQ	42778	0.71138	-98.3			
27RV 4	BQ	42778	0.64640	-90.9			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
DRAINS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
15DR 1	BS	72677	0.36059	.	0.33271	26.0	10.9
15DR 1	BQ	72677	0.36207	-0.4			
15DR 1	BQ	72677	0.27546	26.8			
22DR 8	BS	70977	0.00483	.	0.00562	28.0	14.0
22DR 8	BQ	71177	0.00640	-28.0			
27DR 35	BS	102577	0.11414	.	0.16358	60.4	30.2
27DR 35	BQ	103177	0.21301	-60.4			
13DR 4	BS	41078	0.02771	.	0.04099	64.8	32.4
13DR 4	BQ	41078	0.05426	-64.8			
13DR 5	BS	41078	0.00897	.	0.00890	84.1	26.2
13DR 5	BQ	41078	0.01261	-33.8			
13DR 5	BQ	41078	0.00513	54.4			
35DR 11	BS	92077	0.03018	.	0.03126	90.8	27.4
35DR 11	BQ	92077	0.01761	52.6			
35DR 11	BQ	92077	0.04598	-41.5			
22DR 23	BS	20678	0.00246	.	0.00295	97.1	28.4
22DR 23	BQ	20678	0.00462	-61.2			
22DR 23	BQ	20678	0.00176	33.1			
36DR 4	BS	113077	0.00428	.	0.00709	98.2	38.5
36DR 4	BQ	113077	0.01124	-89.7			
36DR 4	BQ	113077	0.00574	-29.2			
32DR 8	BS	50278	2.63181	.	1.89172	104.6	49.4
32DR 8	BQ	50278	2.39114	9.6			
32DR 8	BQ	50278	0.65220	120.6			
32DR 9	BS	50278	0.78253	.	3.16103	134.8	79.8
32DR 9	BQ	50578	5.04340	-146			
32DR 9	BQ	50578	3.65716	-129			
1DR 2	BS	101077	0.00000	.	0.00003	143.5	94.7
1DR 2	BQ	101077	0.00004	-161			
1DR 2	BQ	101177	0.00005	-167			
32DR 20	BS	50278	1.11175	.	0.69579	156.8	79.0
32DR 20	BQ	50278	0.95519	15.1			

Continued

TABLE C2-4. (Continued)

QUALITY CONTROL DATA AND SUMMARY STATISTICS
DRAINS

ID	SAMP	DATE	NON-METH LEAK RATE	INDIV % DIFF	MEAN NM LEAK RATE	MAX % DIFF	POOLED STAND DEV
32DR 20	BQ	50578	0.02043	192.8			
17DR 20	BS	20278	0.00391	.	0.01913	173.9	85.6
17DR 20	BQ	20278	0.02720	-150			
17DR 20	BQ	20278	0.01654	-124			
17DR 20	BC	20278	0.00451	-14.2			
17DR 20	BQ	20378	0.01285	-107			
17DR 20	BQ	20378	0.02536	-147			
17DR 20	BQ	20378	0.03717	-162			
17DR 20	BQ	20378	0.03540	-160			
17DR 20	BQ	20378	0.01916	-132			
17DR 20	BQ	20378	0.00917	-80.4			
17DR 19	BS	20278	0.00034	.	0.00619	184.1	107
17DR 19	BQ	20278	0.00219	-147			
17DR 19	BQ	20378	0.01050	-186			
17DR 19	BQ	20378	0.01173	-189			

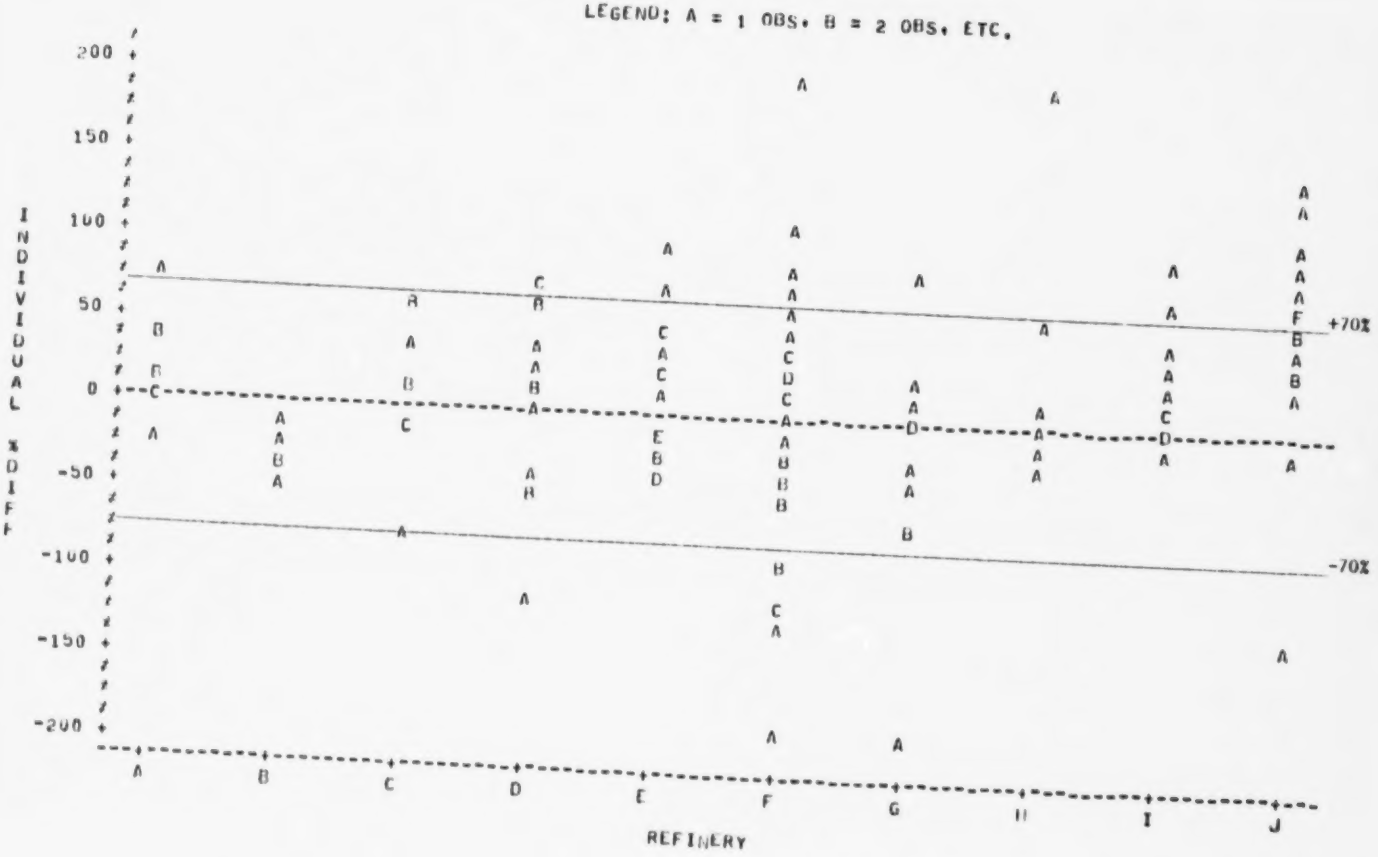


FIGURE C2-14. Percent Difference Between Repeat Samples by Refinery - Valves

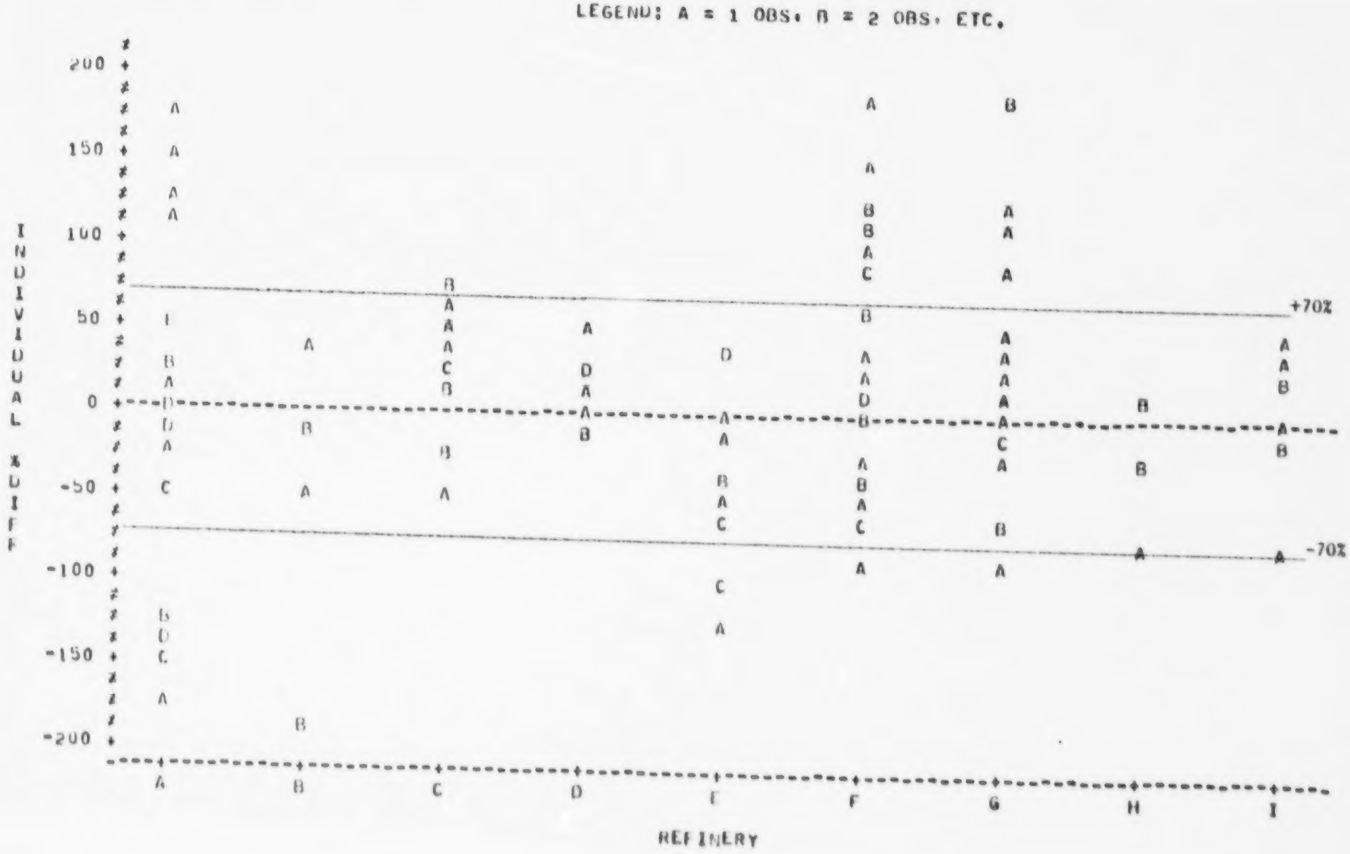


Figure C2-15. Percent Difference Between Repeat Samples by Refinery - Pump Seals

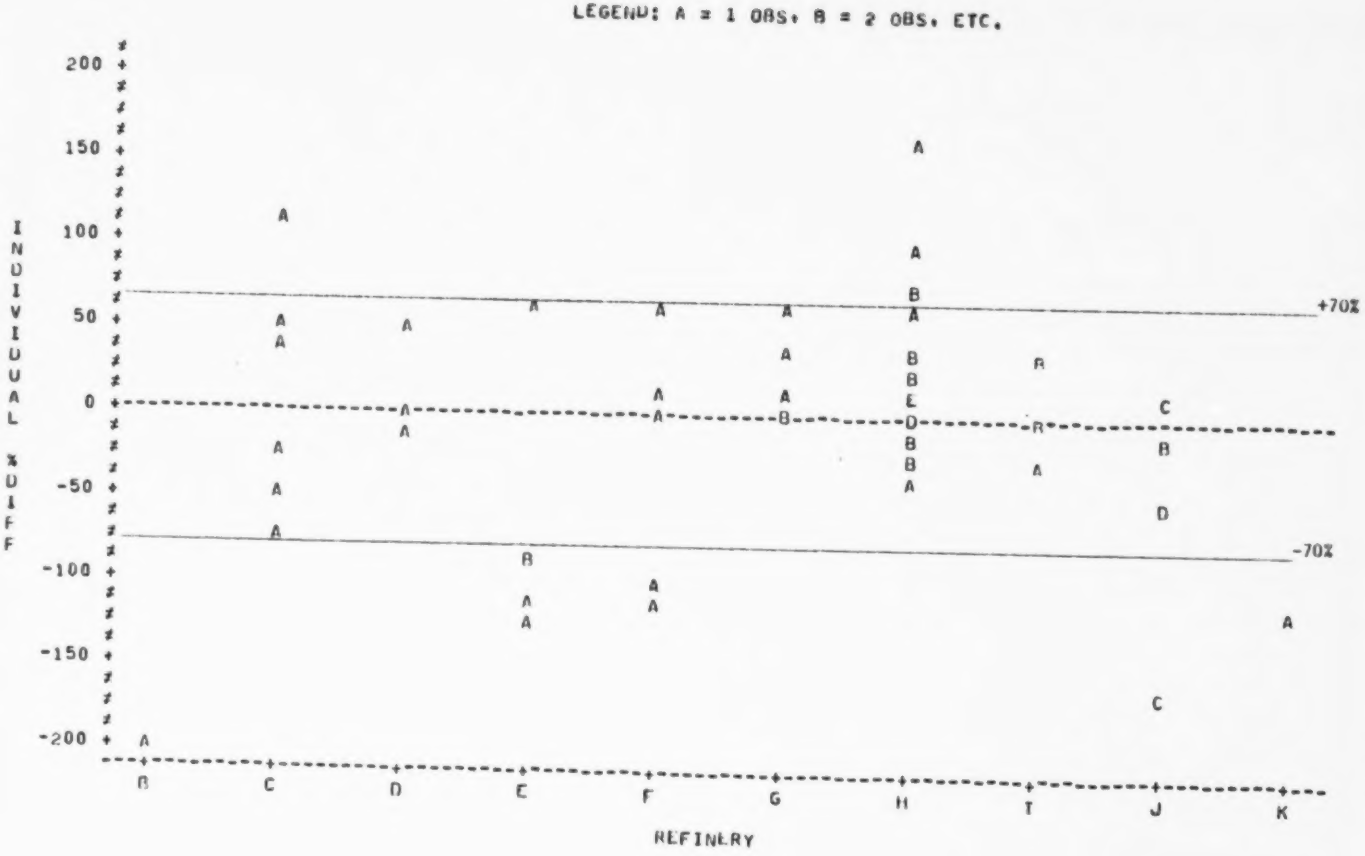


Figure C2-16. Percent Difference for Repeat Samples by Refinery - Compressor Seals

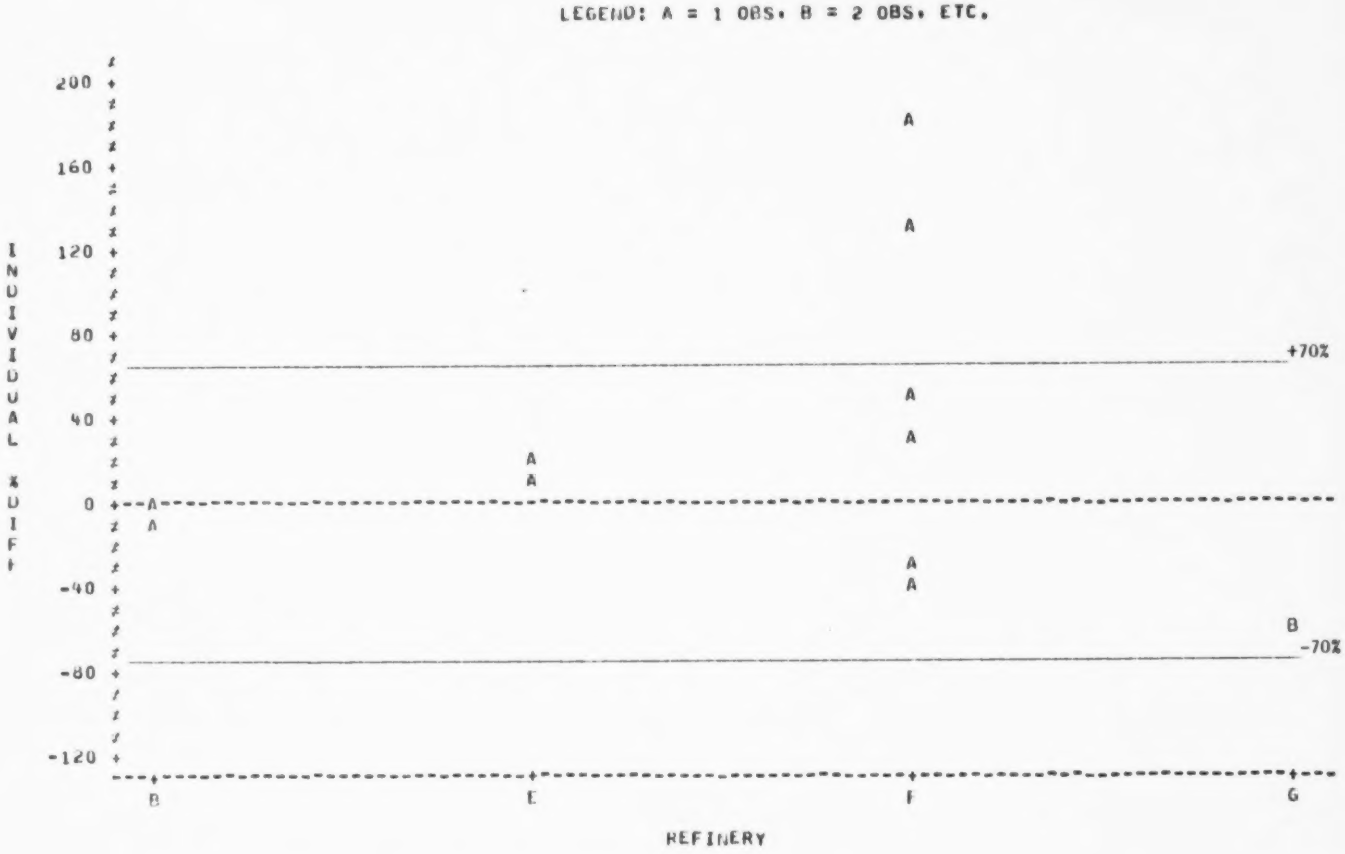


Figure C2-17. Percent Difference for Repeat Samples by Refinery - Flanges

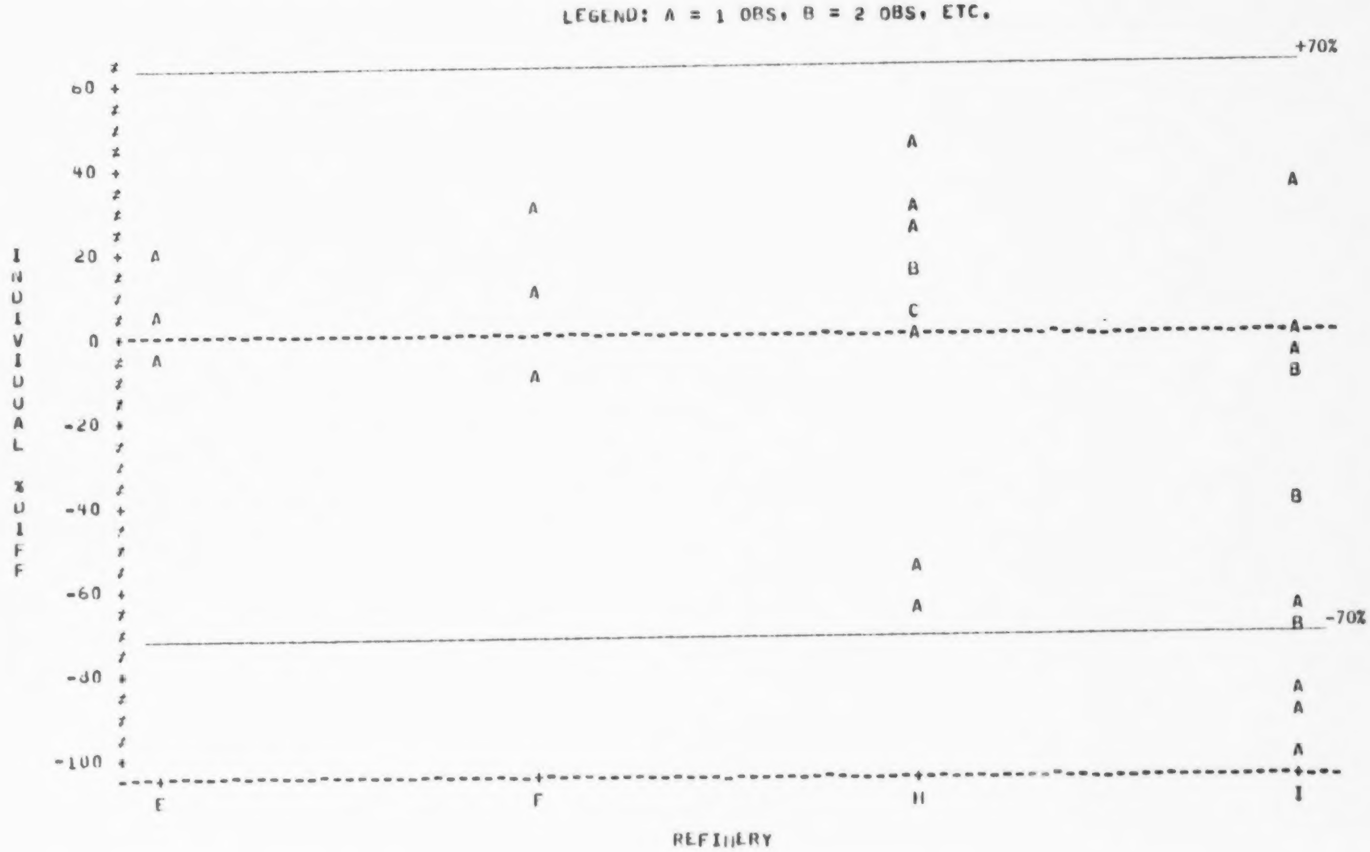


Figure C2-18. Percent Difference for Repeat Samples by Refinery - Relief Valves

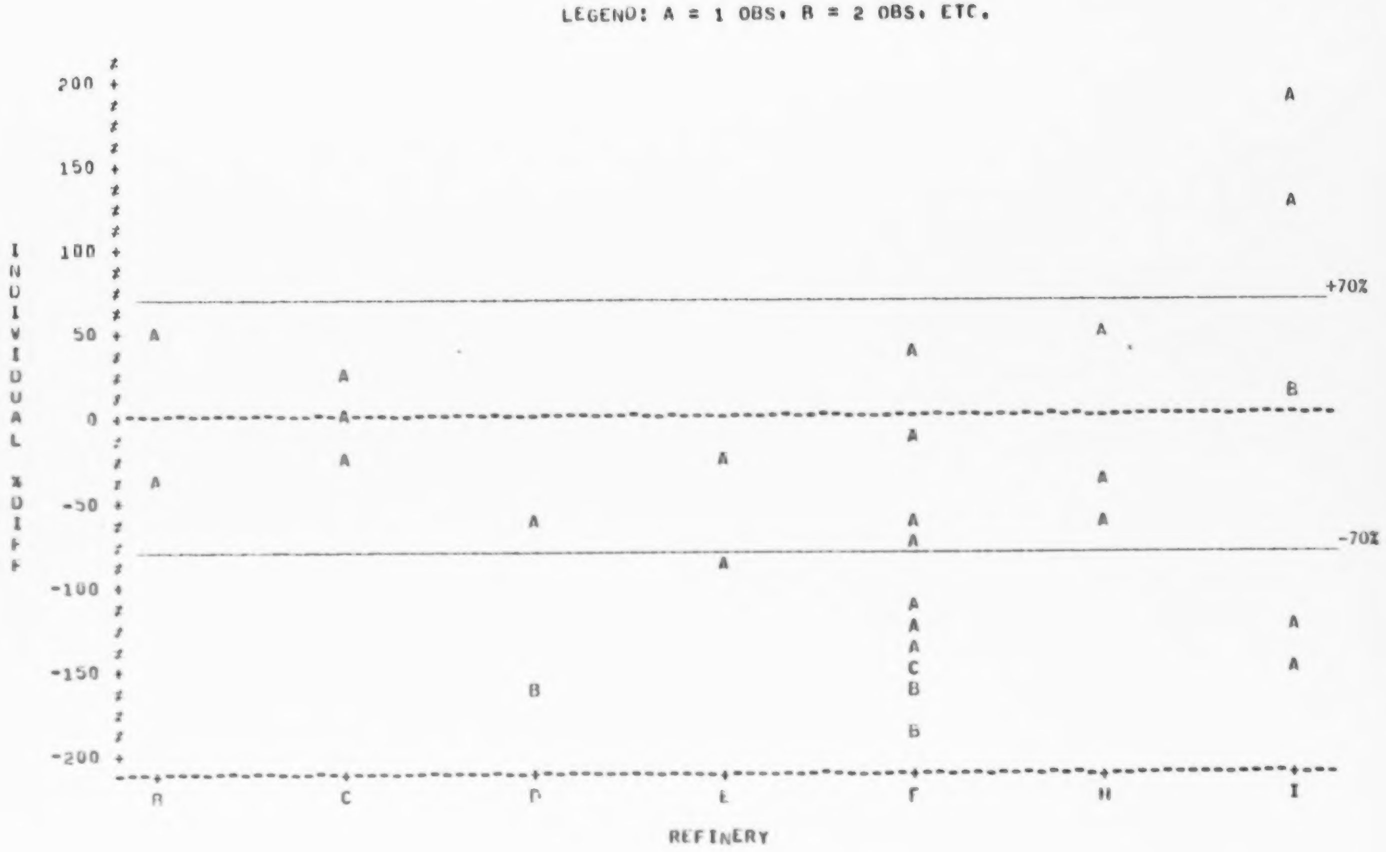


Figure C2-19. Percent Difference for Repeat Samples by Refinery - Drains

refineries for each of the types of sources bagged. Figures C2-20 through C2-25 show these same percent differences plotted versus the average leak rate of the samples from each source. Control limits of ± 70 percent are included on these plots. A maximum 70 percent difference between samples was the original goal for the baggables sampling and analysis procedure. As can be seen, a significant number of checks were outside these limits. Leak rates from drains were especially nonrepeatable. The leak rates appeared to vary considerably with time. In addition, the sampling technique for drains was not as reliable as that for other baggable sources. It was difficult to insure that additional emissions were not induced by the sampling procedure. Frequency distributions of the percent differences for valves and pump seals are shown in Figures C2-26 and C2-27.

Figure C2-28 shows a plot of the pooled standard deviation for the repeat samples versus the average leak rate of the original and quality control samples. Since the standard deviation is obviously related to the concentration level, percent standard deviations were computed. The percent standard deviations are plotted versus the mean leak rate in Figure C2-29. The percent standard deviation appears fairly constant for all levels with a slightly larger percent difference for leak rates less than 0.01 lbs/hr.

Table C2-5 summarizes the statistical analysis of the repeat QC samples. The variability for drains is significantly higher than the other sources while the variability for relief valves is significantly less. The other sources have a standard deviation averaging about 40 percent, or a confidence limit based on a single test of ± 80 percent.

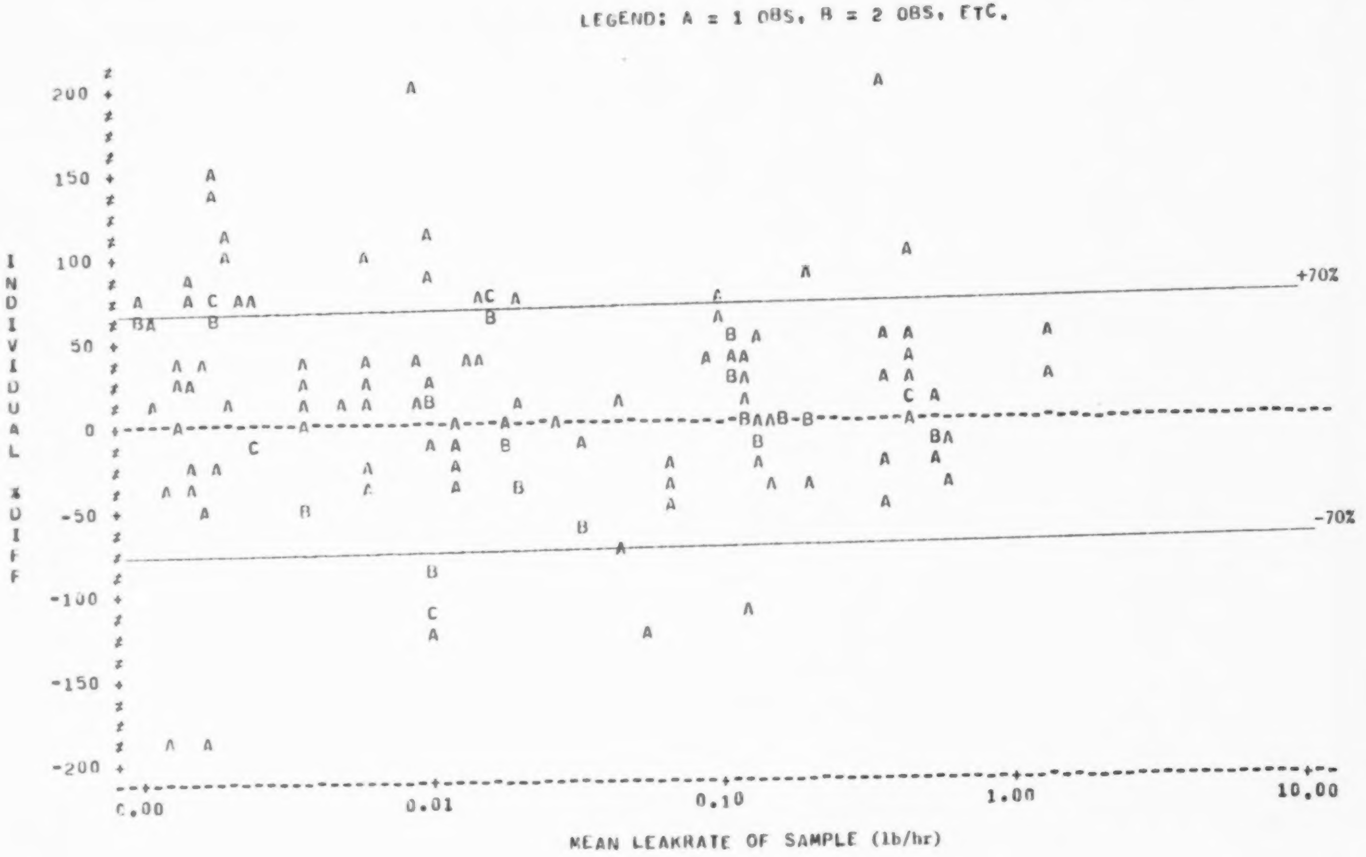


Figure C2-20. Percent Difference for Repeat Samples Versus Mean Leak Rate - Valves

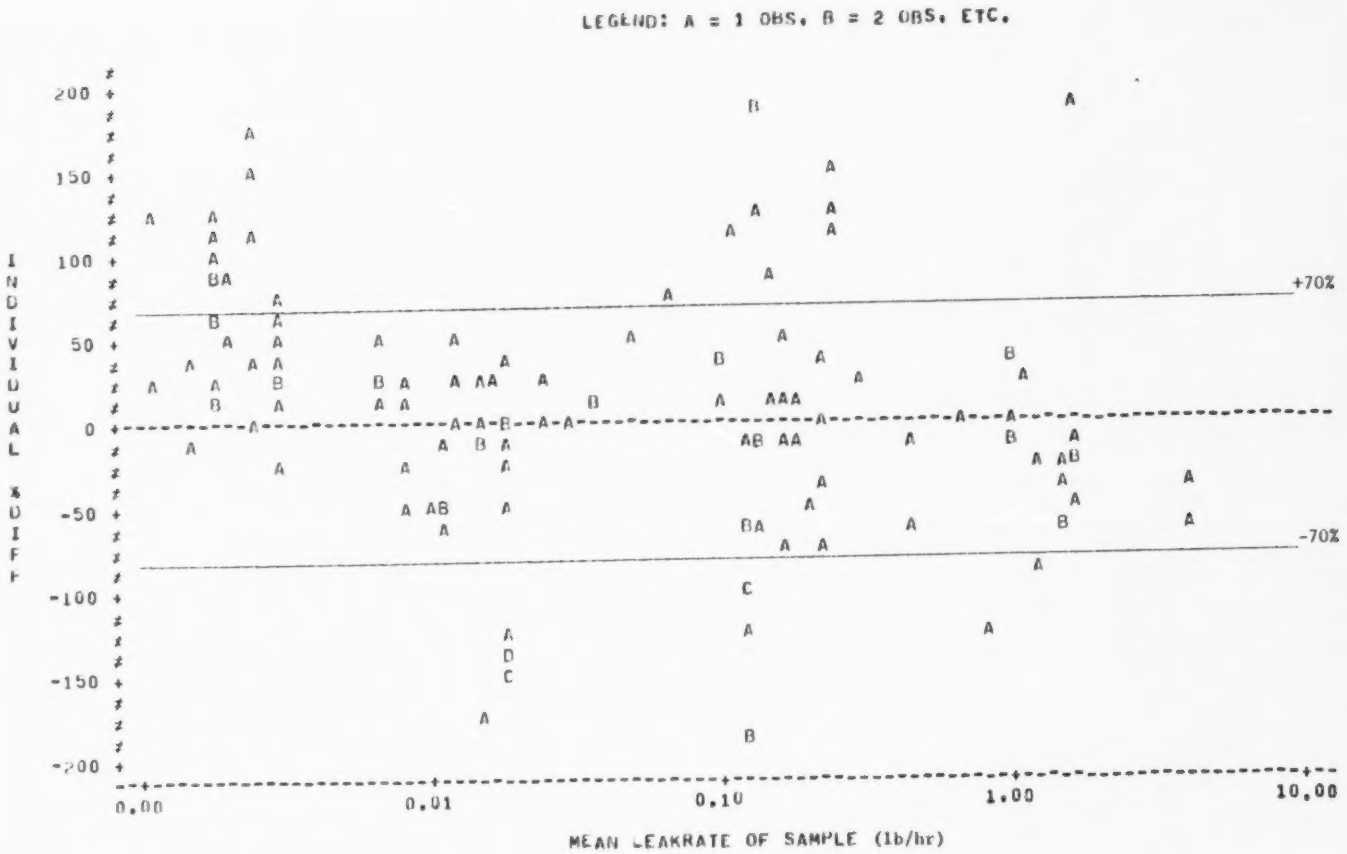


Figure C2-21. Percent Difference for Repeat Samples Versus Mean Leak Rate - Pump Seals

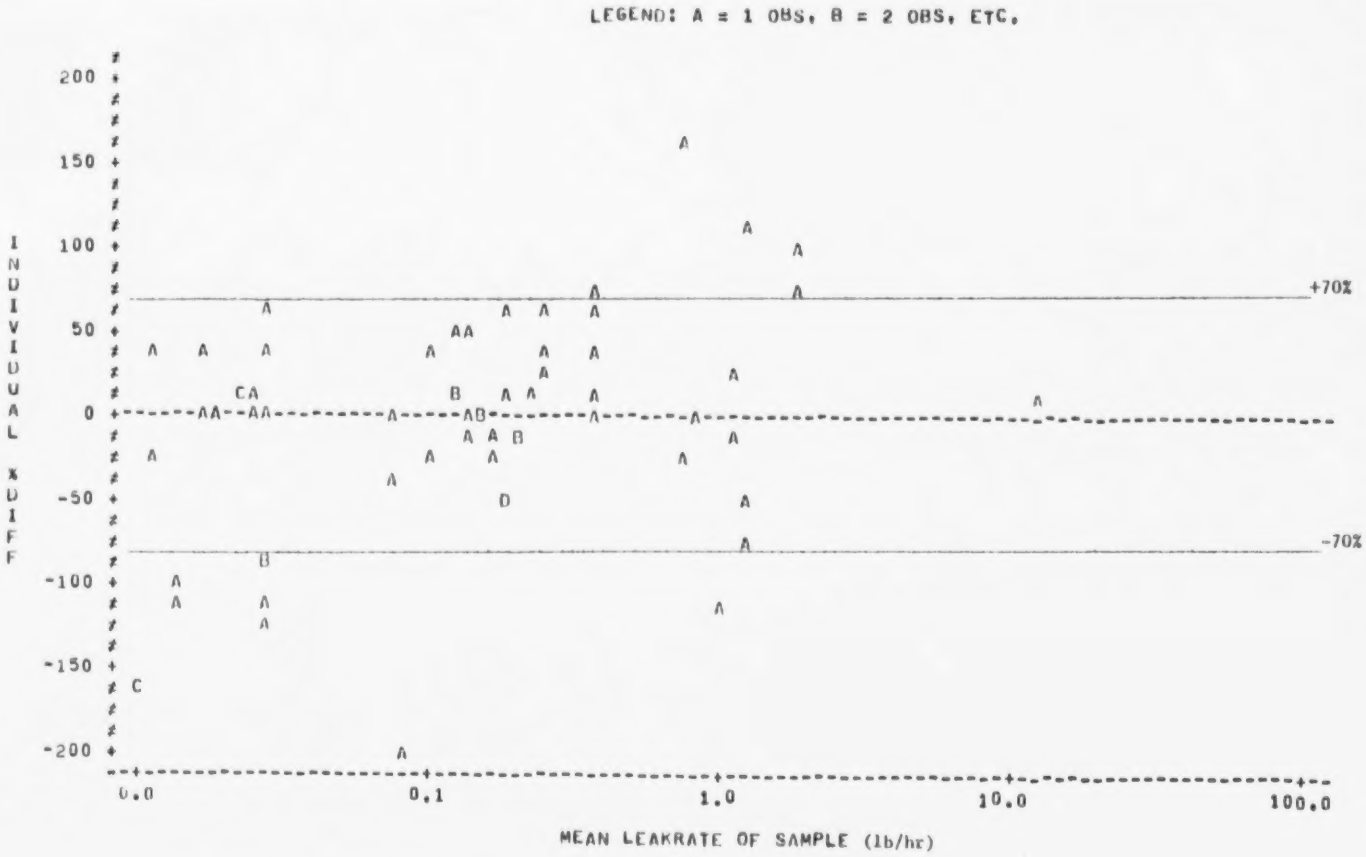


Figure C2-22. Percent Difference for Repeat Samples Versus Mean Leak Rate - Compressor Seals

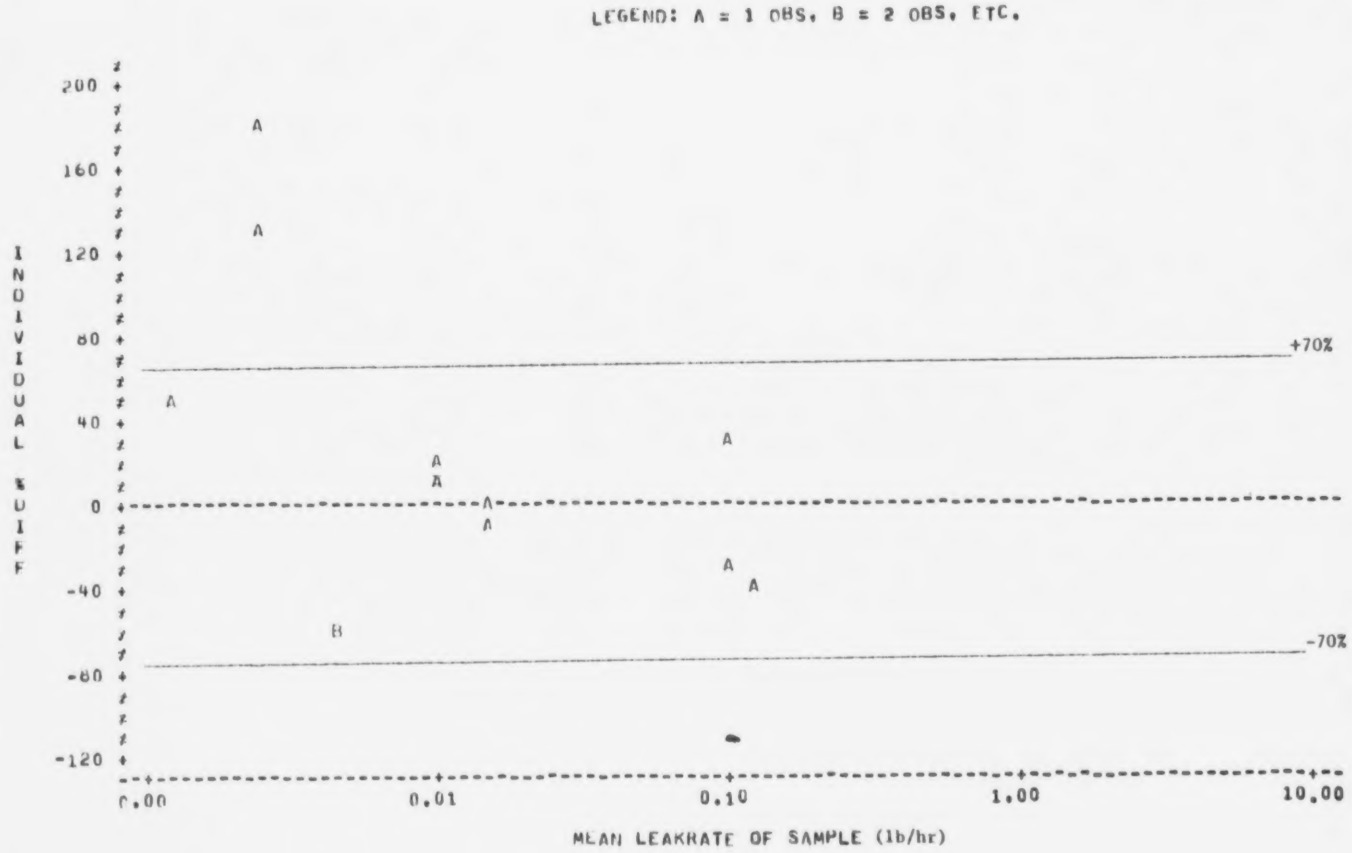


Figure C2-23. Percent Difference for Repeat Samples Versus Mean Leak Rate - Flanges

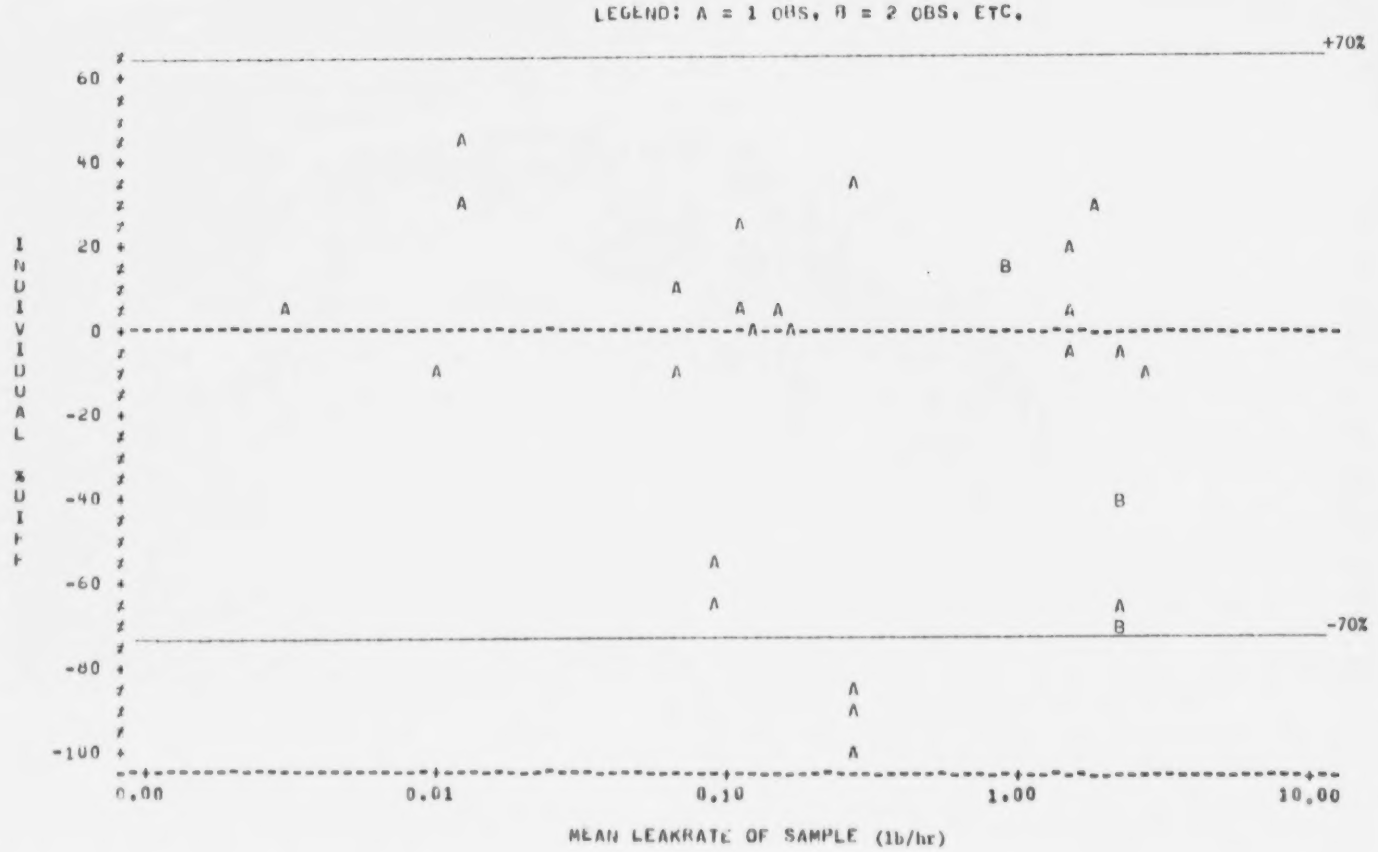


Figure C2-24. Percent Difference for Repeat Samples Versus Mean Leak Rate - Relief Valves

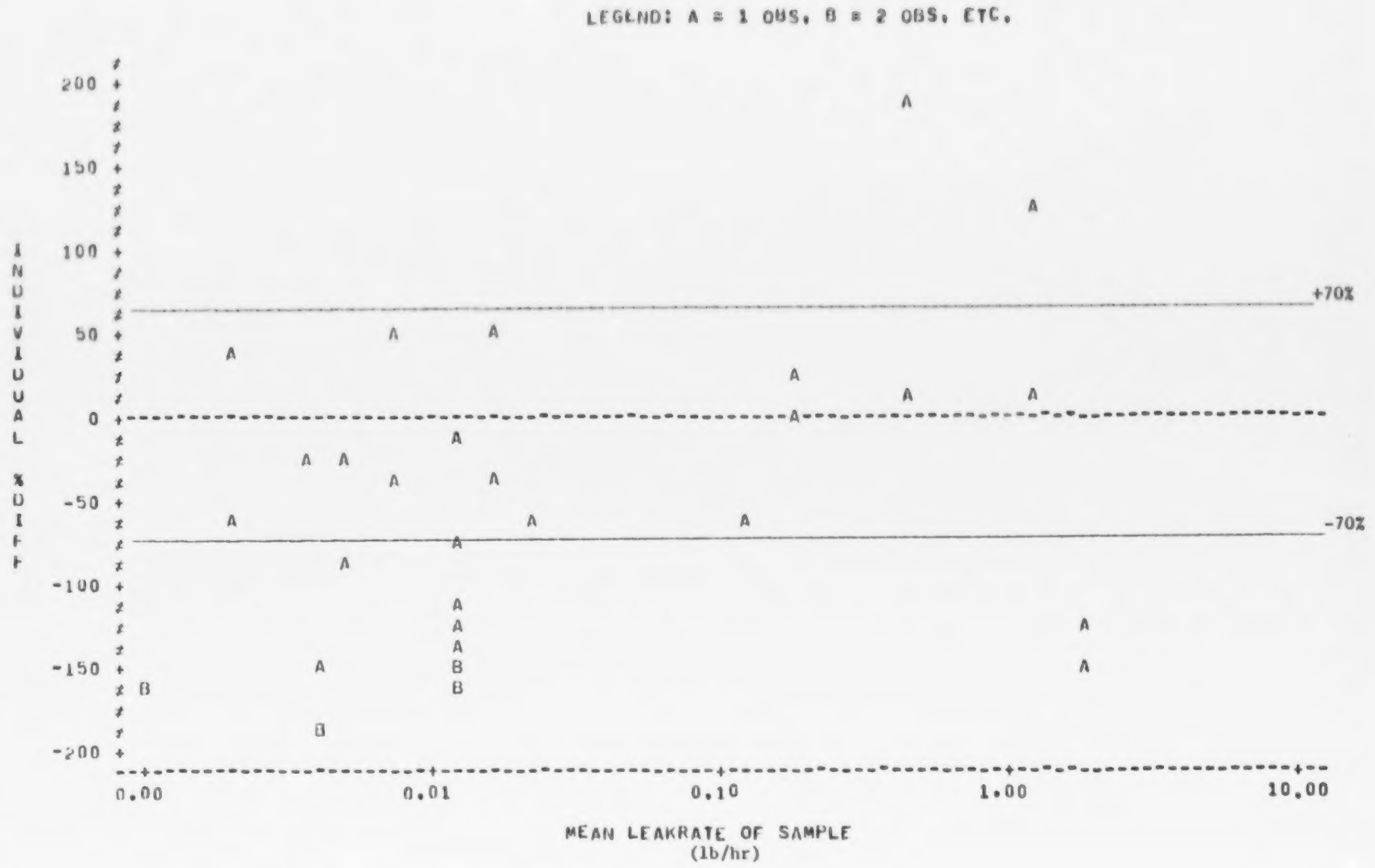


Figure C2-25. Percent Difference for Repeat Samples Versus Mean Leak Rate - Drains

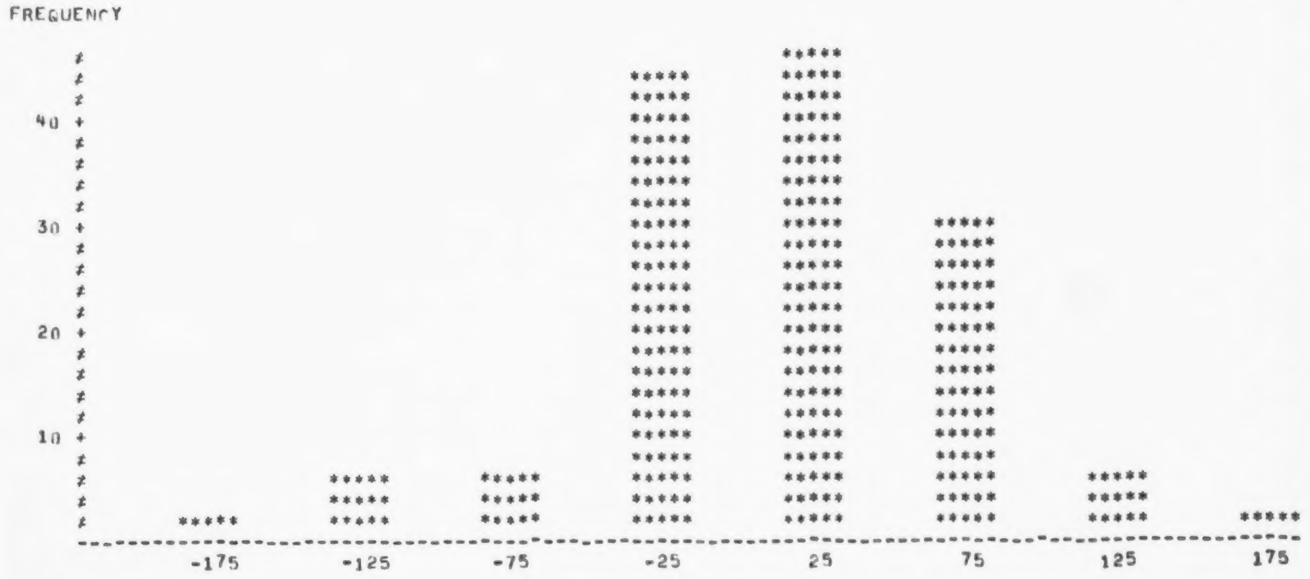


Figure C2-26. Frequency Bar Chart for Percent Differences Between Samples - Valves

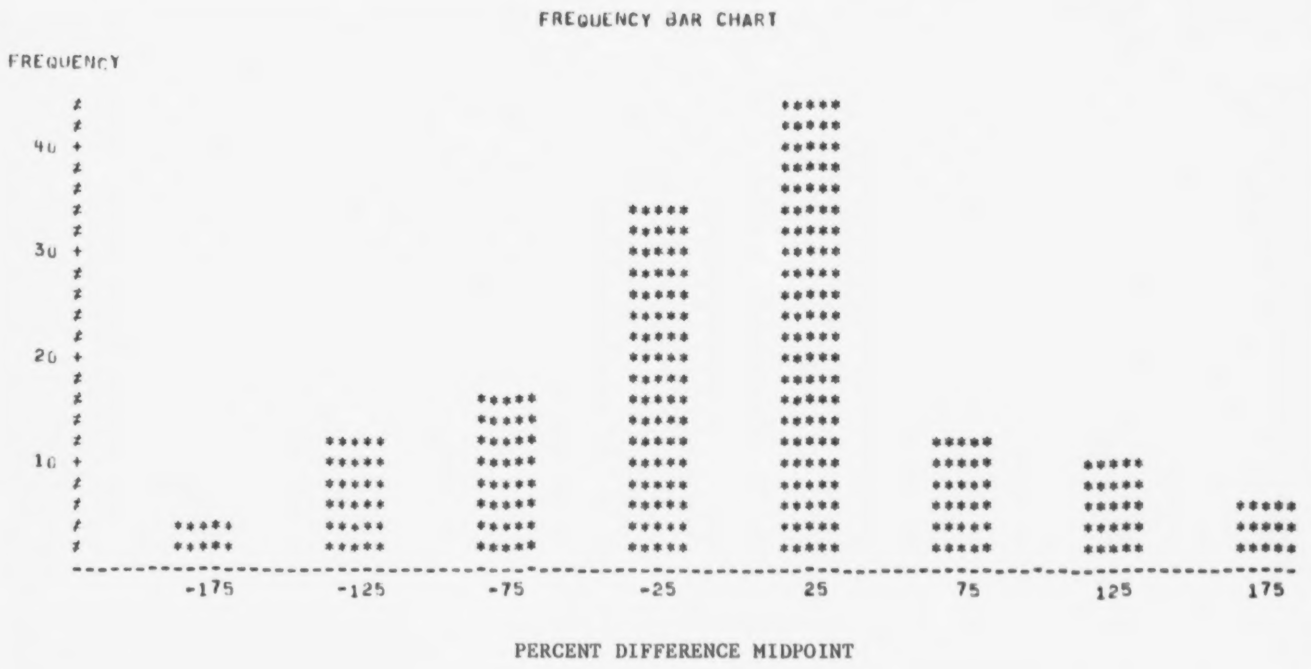


Figure C2-27. Frequency Bar Chart for Percent Differences Between Samples - Pump Seals

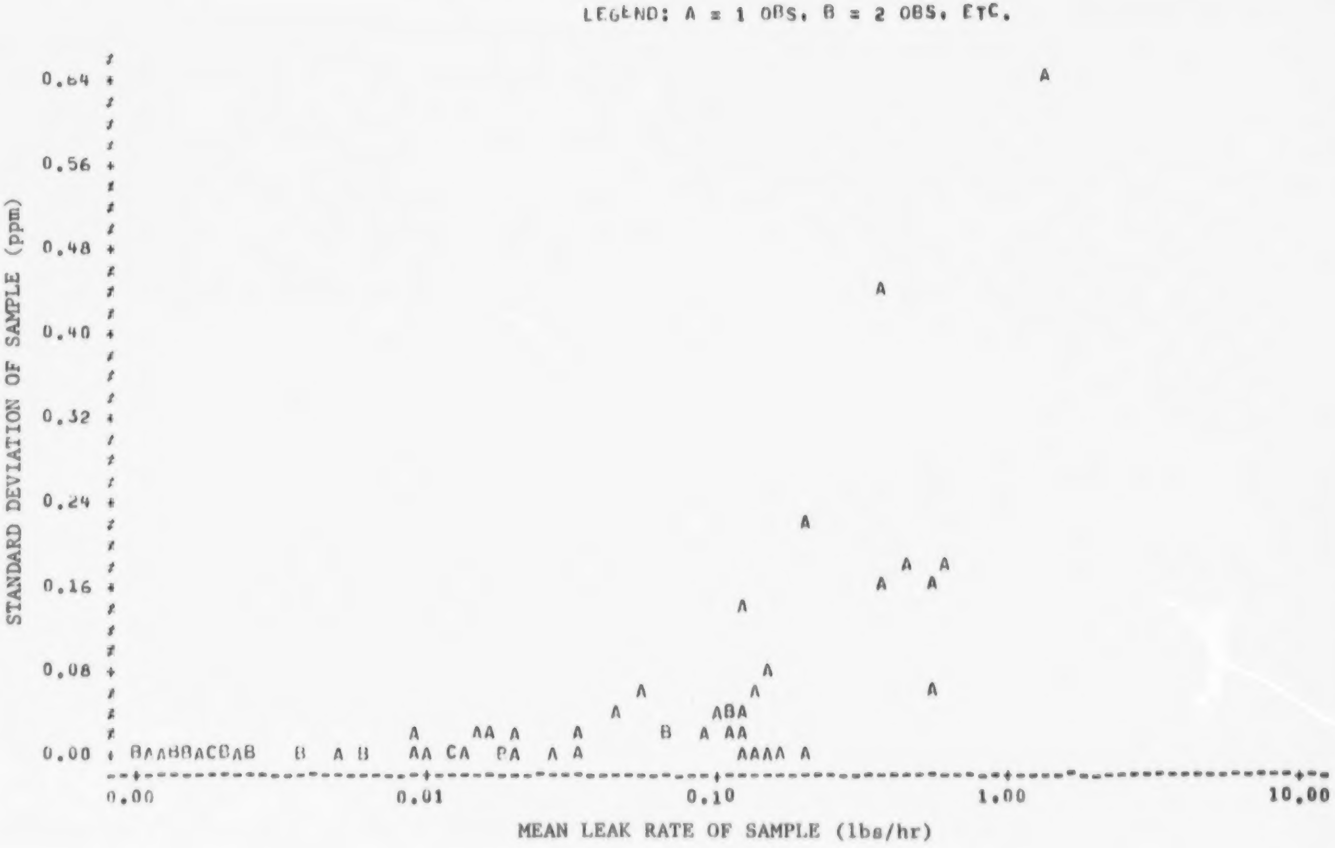


Figure C2-28. Standard Deviation of Repeat Samples Versus Mean Leak Rate - Valves

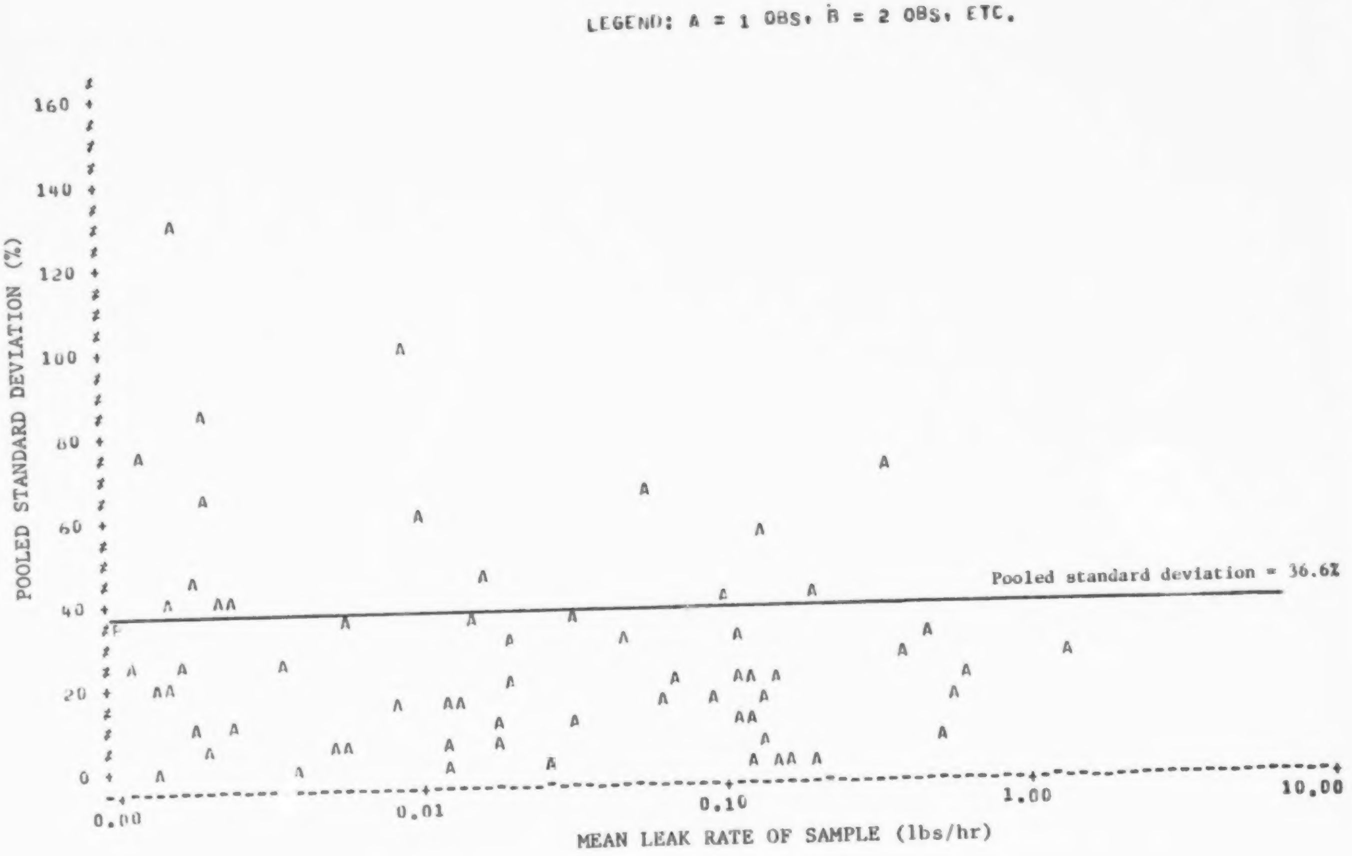


Figure C2-29. Percent Standard Deviation Between Samples Versus Mean Leak Rate - Valves

TABLE C2-5. SUMMARY OF BAGGABLE LEAK RATE QUALITY CONTROL SAMPLE

Source Type	Number of Sources With QC	Total QC Samples	Average Percent Difference[1]	Standard Deviation of Sampling/Analysis,[2] Short-Term Variation	95 Percent Reproducibility of Sampling/Analysis,[3] Short-Term Variation	90 Percent Confidence Interval About A Sample Test Result[4]
Valves	65	137	37.8	36.6	101.4%	± 71.7%
Pump Seals	62	133	44.7	41.9	116.2%	± 82.2%
Compressor Seals	40	66	39.5	38.1	105.6%	± 74.4%
Flanges	7	12	40.0	39.1	108.2%	± 76.6%
Relief Valves	16	30	18.5	19.5	54.0%	± 38.2%
Drains	14	33	71.1	59.1	163.7%	±115.8%
OVERALL	204	411	41.9	40.7	112.8%	± 79.8%

[1] Average % difference - average of pooled percent differences for each soure with QC sample.
Where: % diff = [original - QC leak]/(average of original and QC leak).

[2] Standard deviation of sampling/analysis short-term variations - estimated standard deviation of the sampling and analyses procedures for nonmethane hydrocarbons. Estimated from the pool individual percent differences for each QC sample.

[3] 95 percent reproducibility of sampling/analysis short-term variations - quantity that will be exceeded only about 5 percent of the time by the difference of two test results on a given source under similar process conditions. The quantity is equal to 2.77 × standard deviation.

[4] 90 percent confidence interval - when taken about a single test result, 95 percent of these intervals would be expected to include the "actual" leak rate (without bias considerations); the quantity is equal to 1.96 × standard deviation.

This standard deviation of 40 percent is composed of variation due to analysis, sampling train components, sampling team effect, and inherent short-term variability in the leak rate. In Section 2.2, the standard deviation for the THC analysis was shown to be about 2.4 percent. In Section 2.3 the standard deviation for sampling and analysis of standard gases was shown to be about 17 percent. No significant differences between sampling teams or sampling carts were found, therefore a significant portion of the variability in the leak rate quality control samples is probably due to short-term changes in the leak rate. These changes can be attributed to variations in process conditions, environmental changes, and random variations in the actual leak rate.

Figures C2-30 through C2-32 are examples of the short-term variation in leak rates for selected sources from Table C2-4. Significant changes in relatively short periods of time are obvious from these graphs.

2.4.2 Variance Component Analysis

The variability when measuring the leak rate from a single source can be put in proper perspective for this program by comparing this variation due to short-term variation and sampling/analysis with the total variability of the leak rate data from all sources. Statistical analyses of variance techniques can be used to separate the total variability of the measured leak rate into its various components.

Table C2-6 summarizes the estimation of variance components for the six baggable source types. The variation of the logarithm of the leak rate is broken down into four components of variation:

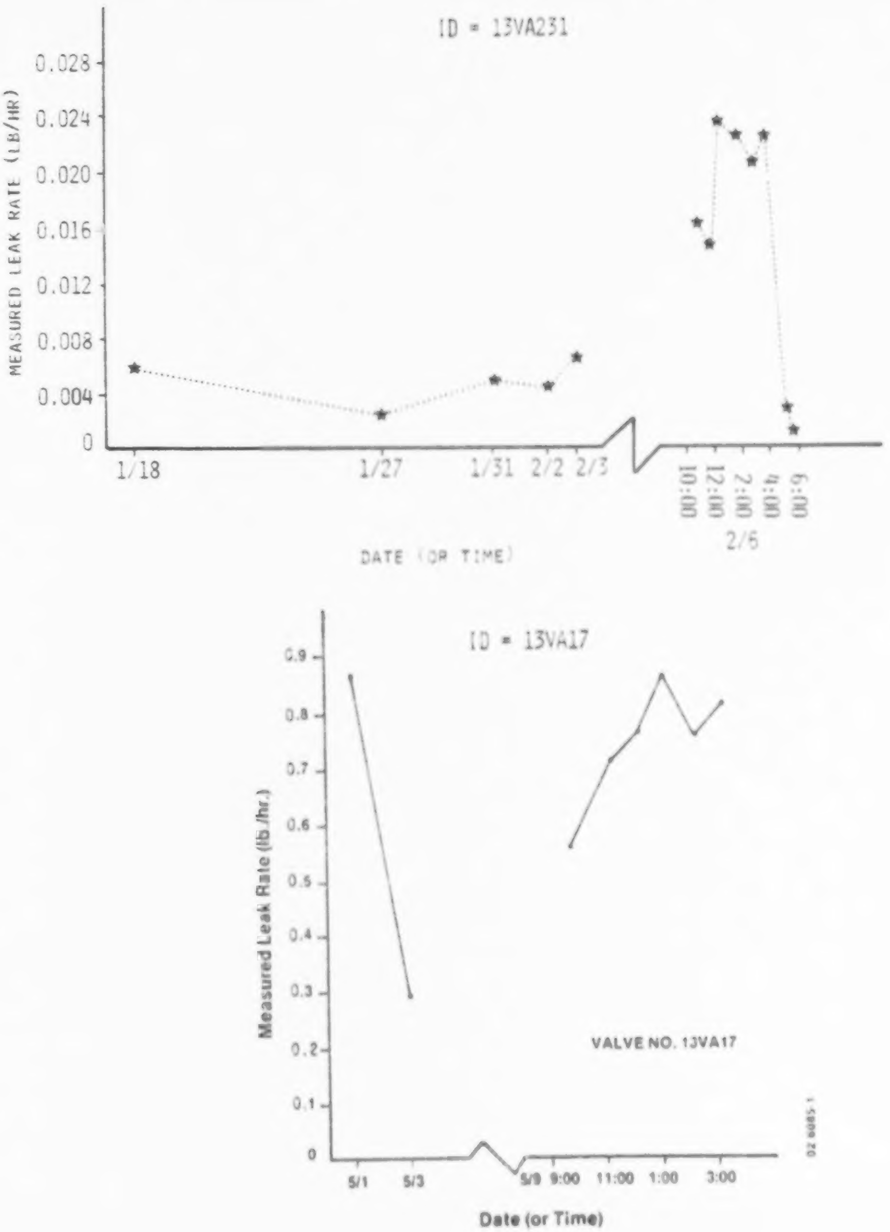


Figure C2-30. Short-Term Variation in Leak Rate - Valves

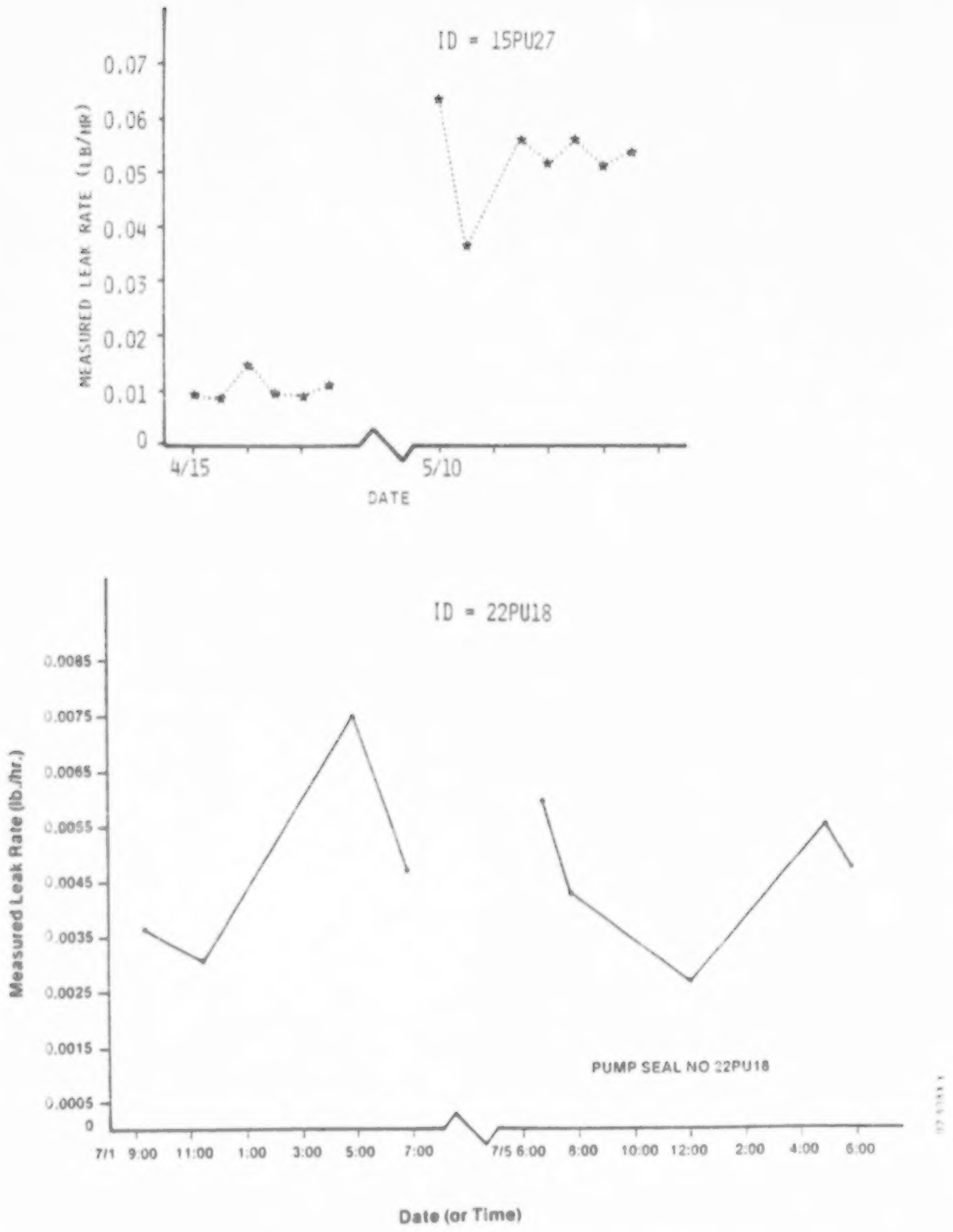


Figure C2-31. Short-Term Variation in Leak Rate - Pumps

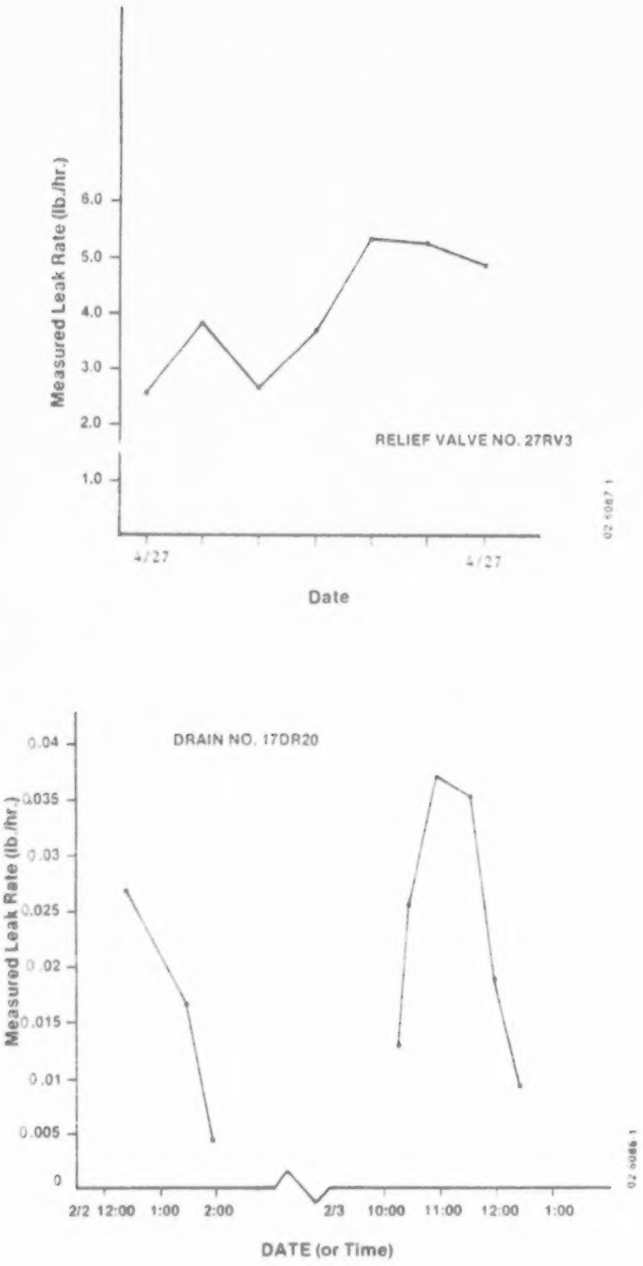


Figure C2-32. Short-Term Variations in Leak Rates - Relief Valves and Drains

TABLE C2-6. VARIANCE COMPONENT ANALYSIS - BAGGABLE SOURCES - LN (LEAK RATE)

SOURCE OF VARIATION	VALVES			PUMP SEALS			FLANGES		
	df*	Variance Component	Percent of Variation	df*	Variance Component	Percent of Variation	df*	Variance Component	Percent of Variation
Refineries	8	-0.174	0.0	8	-0.064	0.0	7	-0.141	0.0
Unit/Refinery	43	0.881	14.2	43	0.666	12.0	16	0.973	0.0
Sources/Unit	573	4.952	80.1	326	4.350	78.2	38	4.591	92.1
Sampling/Analysis Short-term Variations	116	0.351	5.7	137	0.544	9.8	12	0.3[illegible]	7.9
TOTAL	740	6.184	100%	514	5.560	100%	73	4.987	100%

SOURCE OF VARIATION	COMPRESSOR SEALS			RELIEF VALVES			DRAINS		
	df*	Variance Component	Percent of Variation	df*	Variance Component	Percent of Variation	df*	Variance Component	Percent of Variation
Refineries	12	-0.207	0.0	8	0.840	12.7	8	-0.224	0.0
Unit/Refinery	24	3.907	59.0	9	0.822	12.5	23	2.354	37.0
Source/Unit	140	1.927	29.1	40	4.685	71.0	17	2.648	41.6
Sampling/Analysis Short-term Variations	76	0.792	11.9	31	0.250	3.8	34	1.360	21.4
TOTAL	252	6.626	100%	88	6.598	100%	82	6.362	100%

* df = degrees of freedom

- refineries,
- units within a refinery,
- individual sources within a unit, and
- sampling/analysis, short-term variations.

The estimation technique assumes all the components are random, i.e., a random selection of refineries, of units within a refinery, of sources within a unit, and of samples from a particular source. The degrees of freedom in the table is the number of independent pieces of data available for estimating the component of variation.

As can be seen from Table C2-6, the largest percentage of the variation in the log leak rate is due to individual sources except for compressor seals. The variation due to differences between refineries is negligible for all sources except relief valves. The percentage variations due to the sampling and analysis procedures and short-term leak variations range from 3.8 percent for relief valves to 21.4 percent for drains. This component for valves is 5.7 percent. The standard deviation of 40 percent discussed above is not large when compared to the total variability of the leak rate in the data base where leak rates span seven orders of magnitude. Since the emphasis in this program is on overall estimates rather than estimates of individual leak rates, the variability of the sampling and analysis process is certainly acceptable for the program objectives.

3.0 QUALITY CONTROL FOR HYDROCARBON SCREENING PROCEDURE

The screening of sources during this field sampling program was accomplished with sensitive portable hydrocarbon detectors. The principal device used in this study was the J. W. Bacharach Instrument Company "TLV Sniffer." The Century Instrument Company Organic Vapor Analyzer (Model OVA-108) was used for some screening, but not enough data were available for developing correlations. The instruments were calibrated daily with standard mixtures of hexane in air. The OVA-108 and TLV Sniffer give direct readings of hydrocarbon concentrations in ppm by volume.

When screening valves, pumps or compressors, the probe of the hydrocarbon detector was normally placed as close as possible to the intersection of the shaft with the sealing device (0 cm). The probe was held at this location for a minimum of five seconds. The detector reading was recorded. This was repeated at three other points 90 degrees apart around the shaft. The maximum reading was used as the screening value for the sampling criterion. This maximum may not be the true maximum which could be obtained by screening over the whole 360 degrees. Subjective evaluations by the engineers doing the screening indicated that the difference in maximums would not be significant.

Flanges were screened by placing the detector probe at 2-inch intervals all around and right against the outside perimeter of the flange interface. The maximum detector reading was recorded. Drains were similarly screened. The detector probe was placed at 2-inch intervals around the perimeter of the drain. The maximum measured hydrocarbon concentration was recorded.

Relief valves were screened by placing the instrument probe at the valve "horn" exit. The screening value obtained at that point was used as the sampling criterion.

For evaluation purposes, some readings were also obtained five centimeters from the source for all source types.

Appendix A discusses further details of the operation of these hydrocarbon detectors. This section discusses the various quality assurance activities related to the screening devices:

- calibration checks,
- repeatability of screening,
- intra- and inter-screener comparisons,
- relationships between TLV and OVA instruments, and
- screening versus soaping techniques for leak detection.

3.1 Screening Device Calibration Checks

The TLV and OVA instruments were calibrated each day they were used. Standards of 500-525 ppmv and 2,000 ppmv hexane in air were used to get a two point calibration each day. Before a recalibration was made each day, the values obtained from the instrument were recorded. This served two purposes:

- check for instrument damage or malfunction, and

- document the stability of the daily calibration.

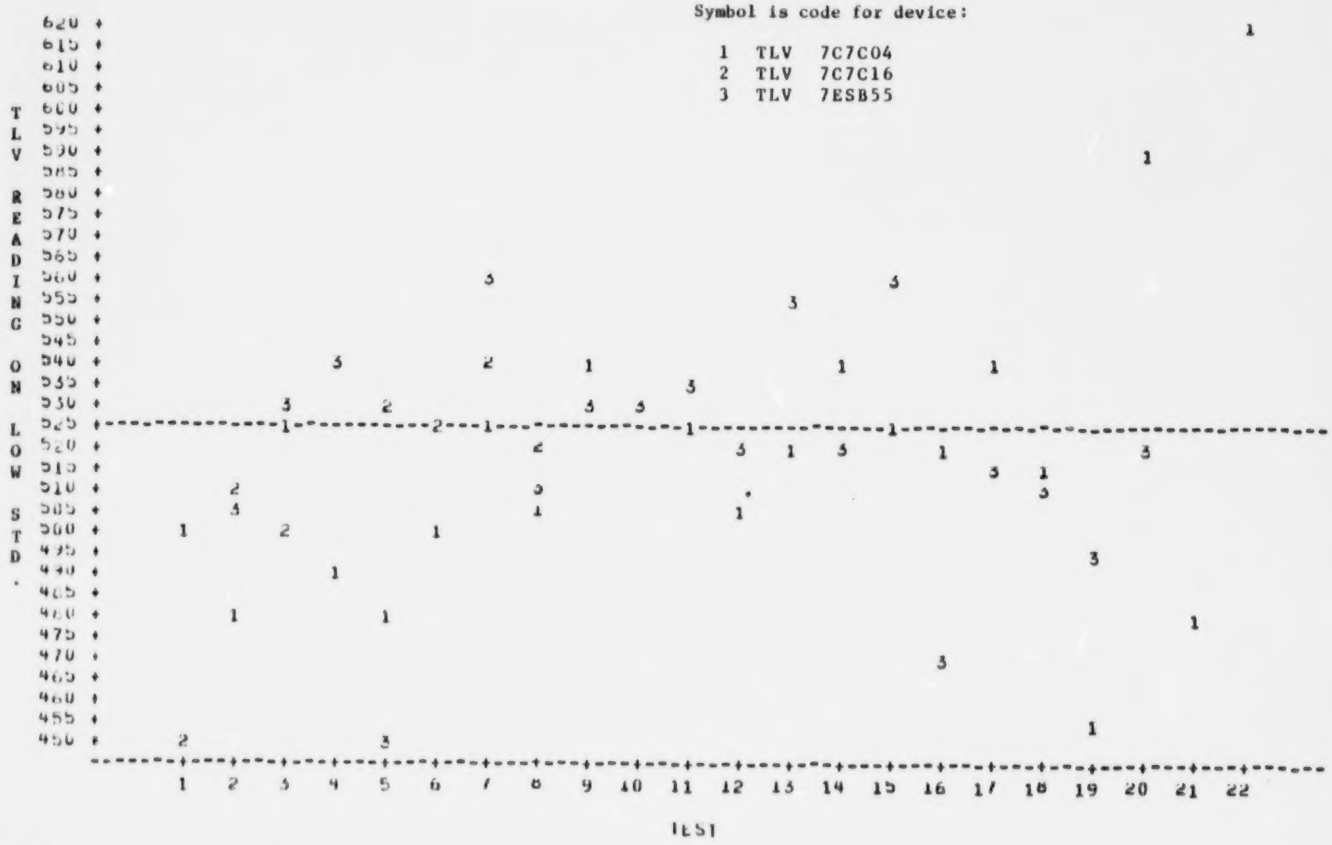
The results of these calibration checks at the last three refineries visited are shown in Figure C3-1 for the lower standard and in Figure C3-2 for the high standard. Three different TLV instruments were used at these refineries. The percent differences from the standards are plotted in Figures C3-3 and C3-4.

Table C3-1 gives a statistical summary of these data. None of the devices gives any indication of a consistent bias (or drift) at either the high or low level. The maximum percent differences found were always less than 20 percent of the known concentration.

Based on these data, it is concluded that the daily calibration of the screening devices at two levels using standard gases was adequate for obtaining consistent, unbiased readings.

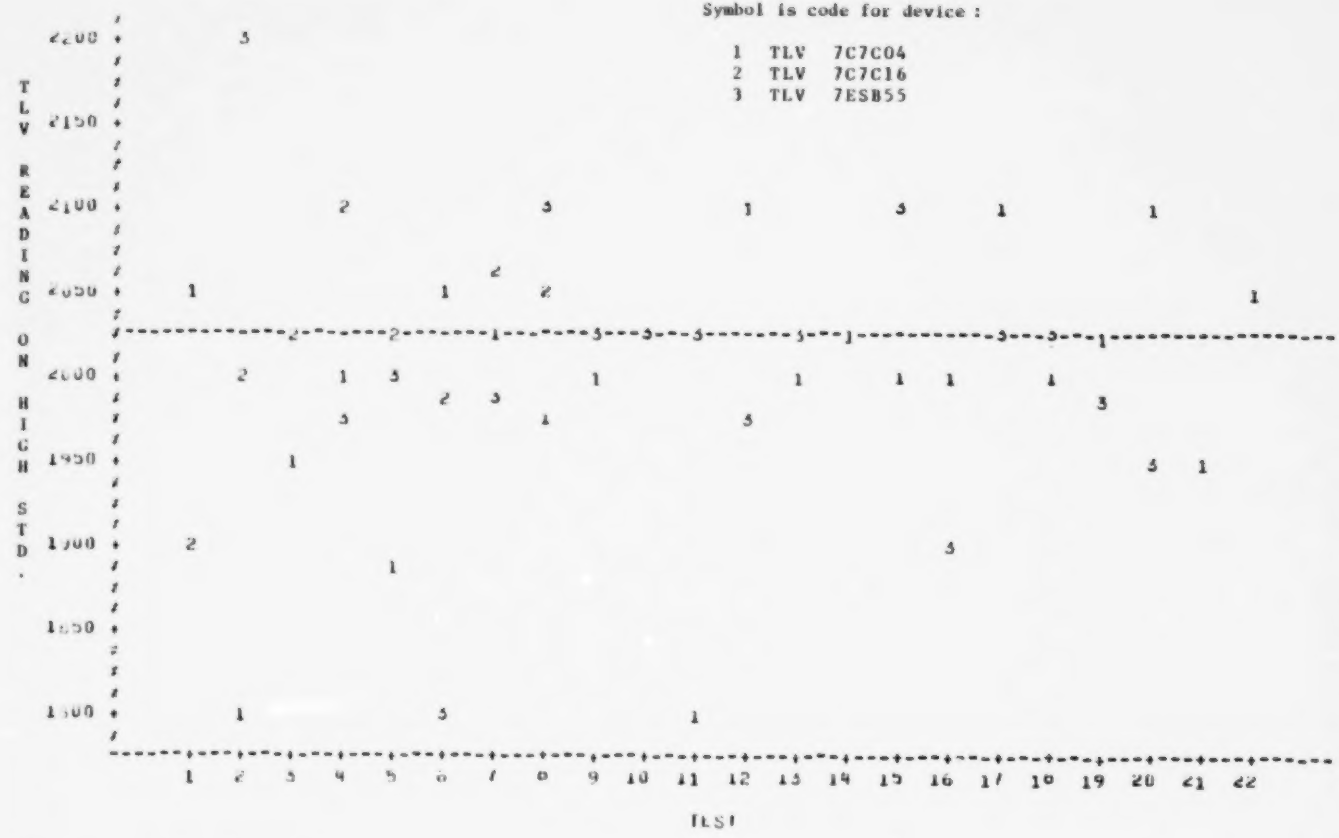
3.2 Repeatability and Reproducibility of the Screening Procedure

Repeatability and reproducibility are estimates of the variation inherent in multiple screenings of individual sources. The 90 percent repeatability is the maximum difference expected between two screenings by the same operator within a short time period (less than 3 minutes). A difference of greater than the repeatability statistic would be expected less than 10 percent of the time. The 90 percent reproducibility is the maximum difference expected between two screenings by different operators within a short time period (less than three minutes).



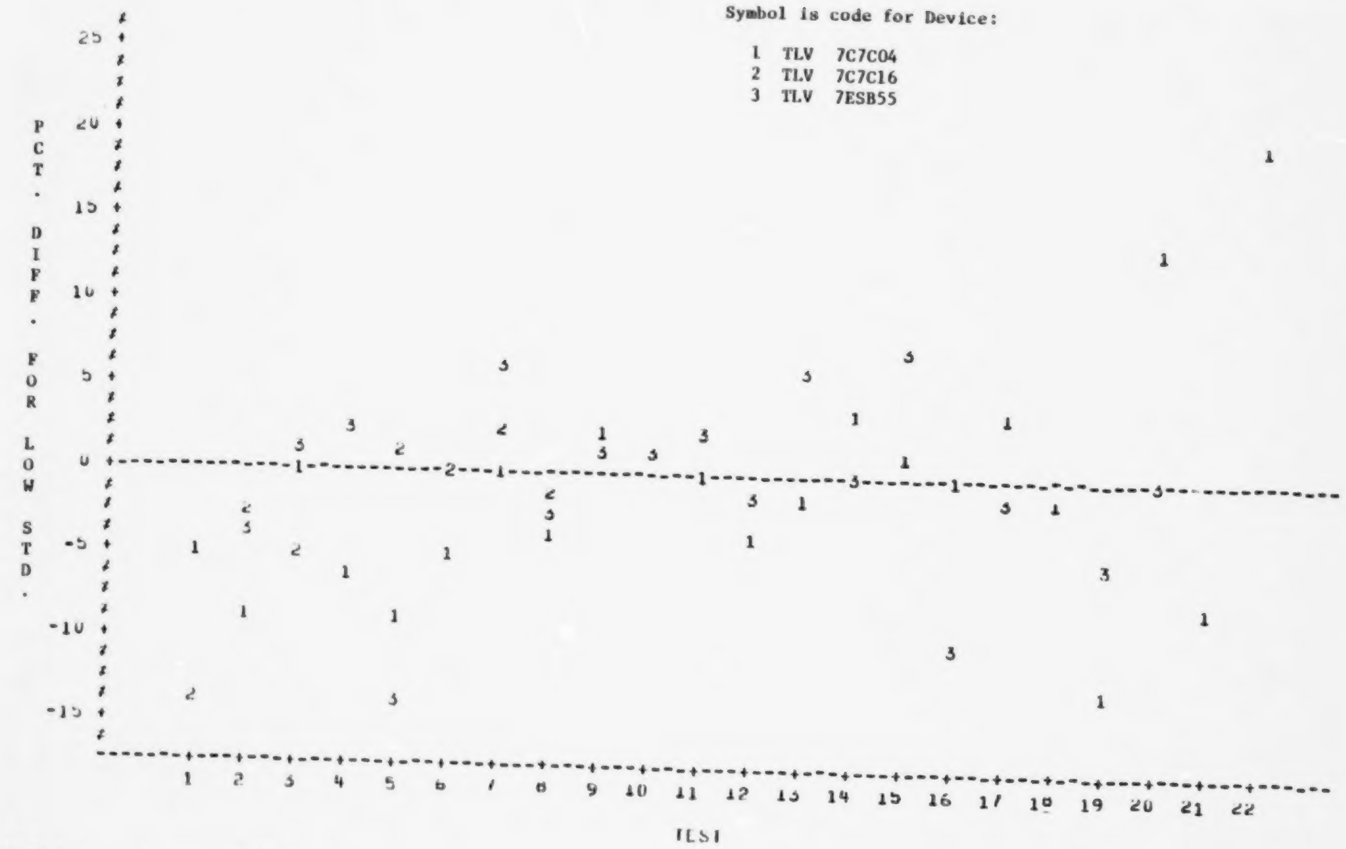
NOTE: 3 OBS HIDDEN

Figure C3-1. Calibration Checks for TLV Sniffer - Low Standard



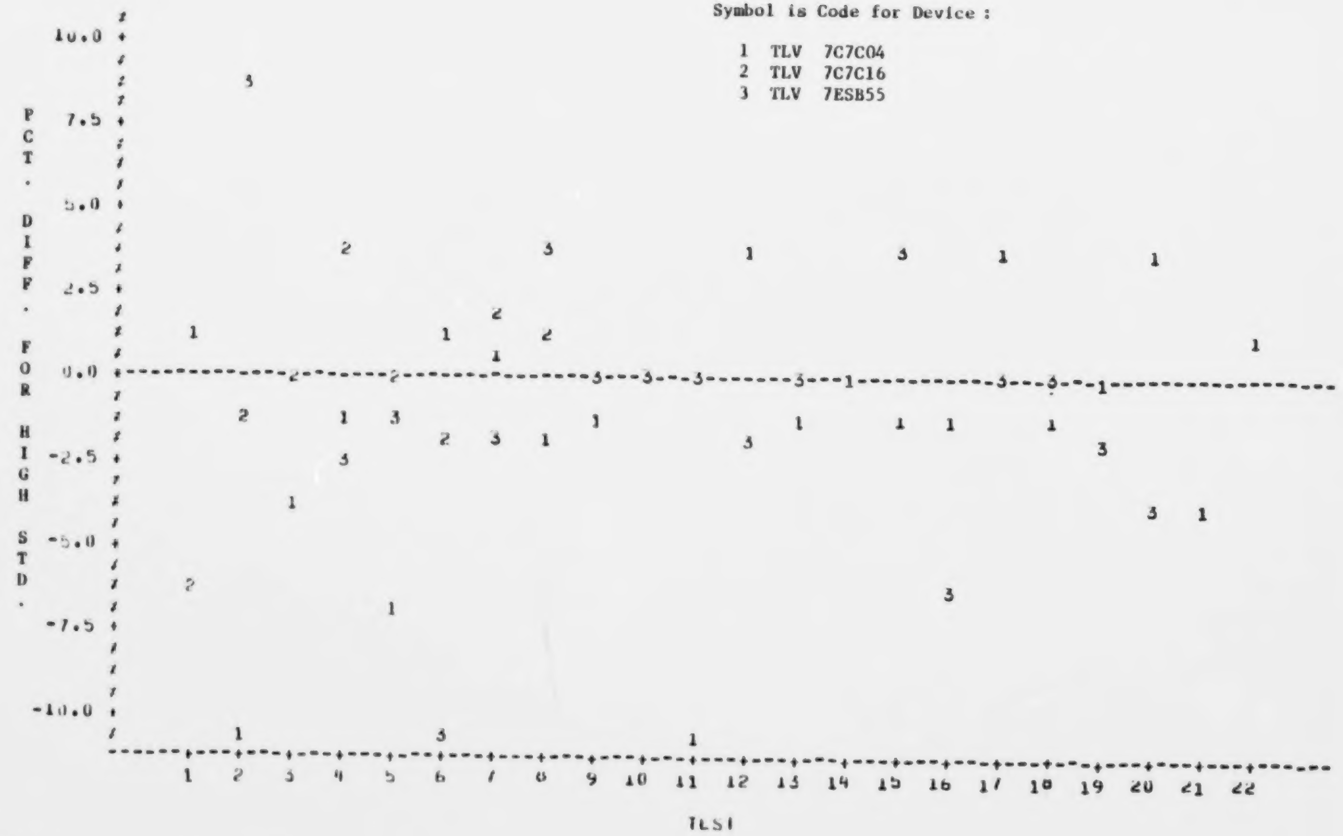
NOTE: 3 OBS HIDDEN

Figure C3-2. Calibration Checks for TLV Sniffer - High Standard



NOTE: 4 OBS HIDDEN

Figure C3-3. Percent Difference for Calibration Checks for TLV Sniffer - Low Standard



NOTE: 3 OBS HIDDEN

Figure C3-4. Percent Differences for Calibration Checks for TLV Sniffer - High Standard

TABLE C3-1. STATISTICAL SUMMARY OF CALIBRATION CHECKS

	Number of Checks	Average Difference (ppm)	Average Percent Difference	Minimum Percent Difference	Maximum Percent Difference	Standard Deviation of % Difference	95% Confidence Interval for Average Percent Difference
Instrument 1							
Low Standard (525 ppm)	21	- 4.4	-0.8	-12.3	19.5	7.3	(-4.1 , 2.5)
High Standard (2023 ppm)	21	-28.0	-1.4	-11.0	3.8	4.1	(-3.3 , 0.5)
Instrument 2							
Low Standard	8	-16.9	-3.2	- 6.1	3.8	5.4	(-7.7 , 1.3)
High Standard	8	- 4.8	-0.2	-14.3	2.9	2.9	(-4.7 , 4.3)
Instrument 3							
Low Standard	20	- 5.3	-1.0	-14.3	7.9	5.2	(-3.4 , 1.4)
High Standard	20	-19.8	-1.0	-11.0	8.7	4.1	(-2.0 , 0.9)

Percent difference = (Measured - Standard) x 100/Standard

The repeatability of the screening process was investigated by performing repeated screenings on the same source by the same operators. The issue of repeatability is again complicated by short term variation in the leak rate. However, an evaluation of the repeatability of the screening procedure is important for future use of the screening devices in standards and maintenance programs. Both the TLV sniffer and the OVA-108 instruments were used to screen at the sources and 5 cm from the source. The absolute value of the percent difference between the duplicate readings is plotted against the mean of the duplicate readings in Figures C3-5 and C3-6 for maximum reading at the source using a TLV and OVA, respectively. Most percent differences are less than 75 percent for the TLV and below 40 percent for the OVA. Figures C3-7 and C3-8 show the same plots of percent difference for TLV and OVA readings at 5 cm from the source. The percent differences for the TLV tend to be higher, indicating that the method is not as repeatable as screening directly at the source.

Quality control studies were run on the TLV sniffer to determine the reproducibility of the measurement method. Between one and five sources at selected refineries were selected with screening values between 200 and 10,000 ppm. Each day that screening was done, at least one team would screen each of the sources. Duplicate readings were sometimes performed on each device, both at the source and 5 cm from the source. Figures C3-9 and C3-10 illustrate typical results obtained from the repeated screenings using the TLV sniffer at the source.

Within a day, the screening results from each team were generally close. A visual comparison of duplicate readings

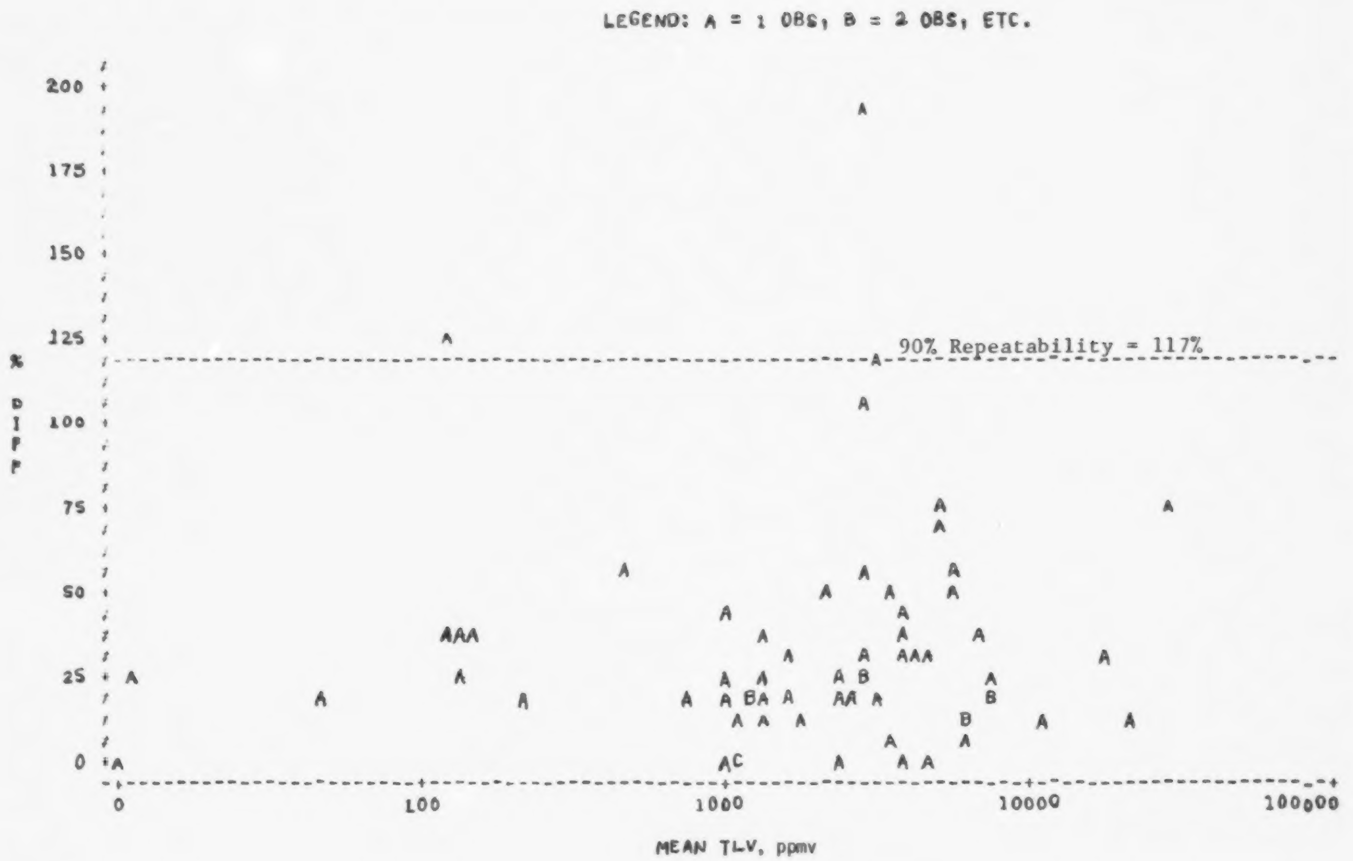


Figure C3-5. Percent Difference Between Duplicate TLV Readings - at the Source

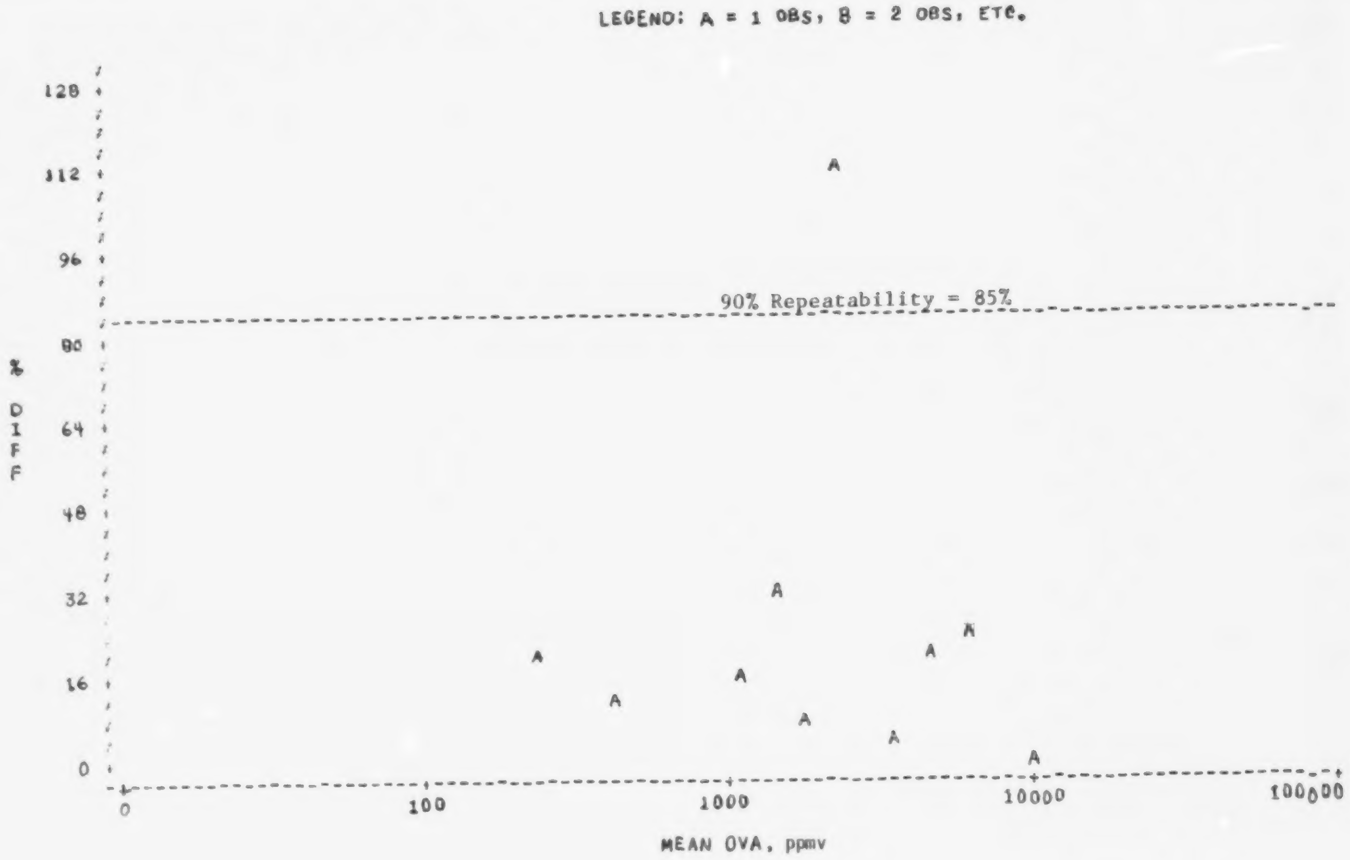


Figure C3-6. Percent Difference Between Duplicate OVA Readings - at the Source

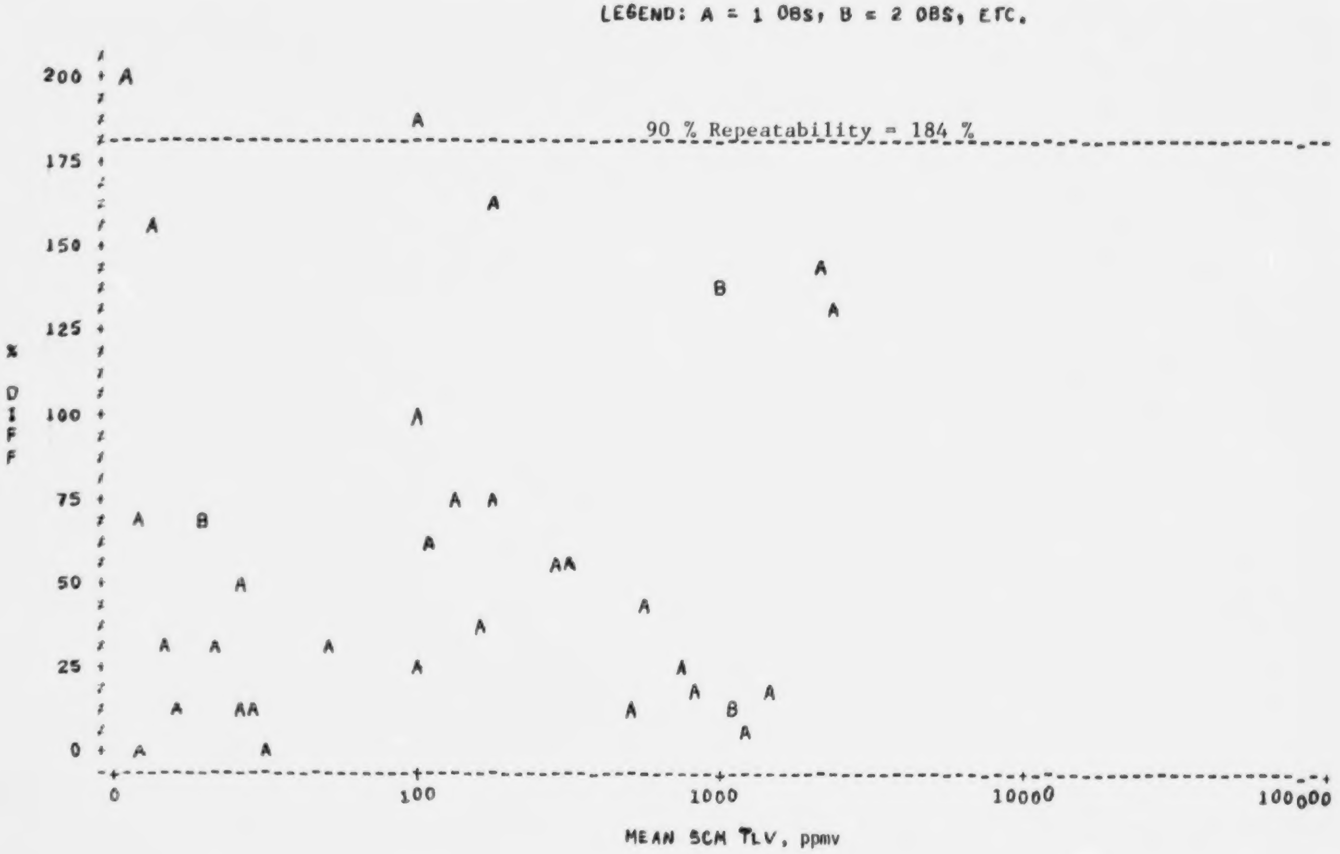


Figure C3-7. Percent Difference Between Duplicate TLV Readings - 5 cm from Source

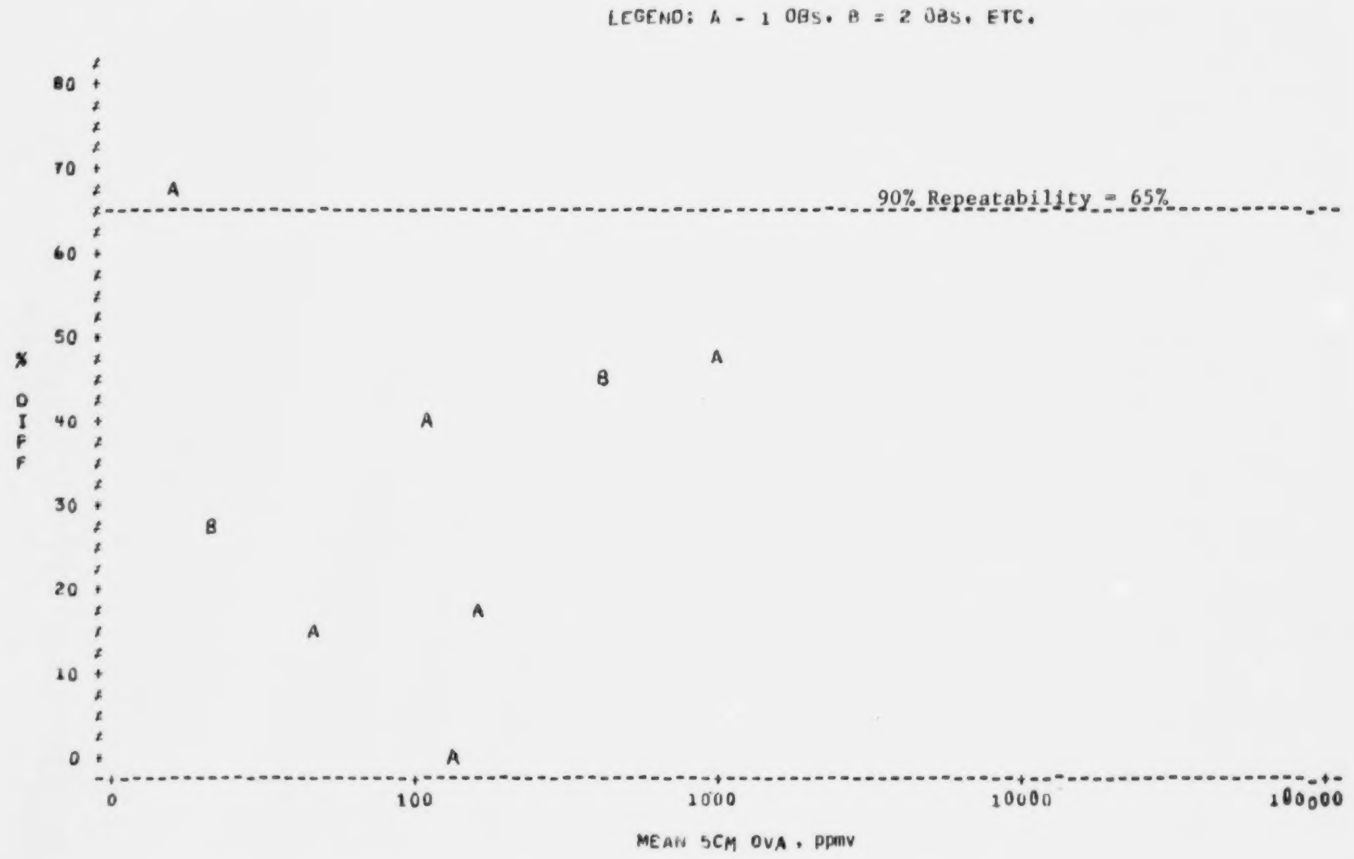


Figure C3-8. Percent Difference Between Duplicate OVA Readings - 5 cm from Source

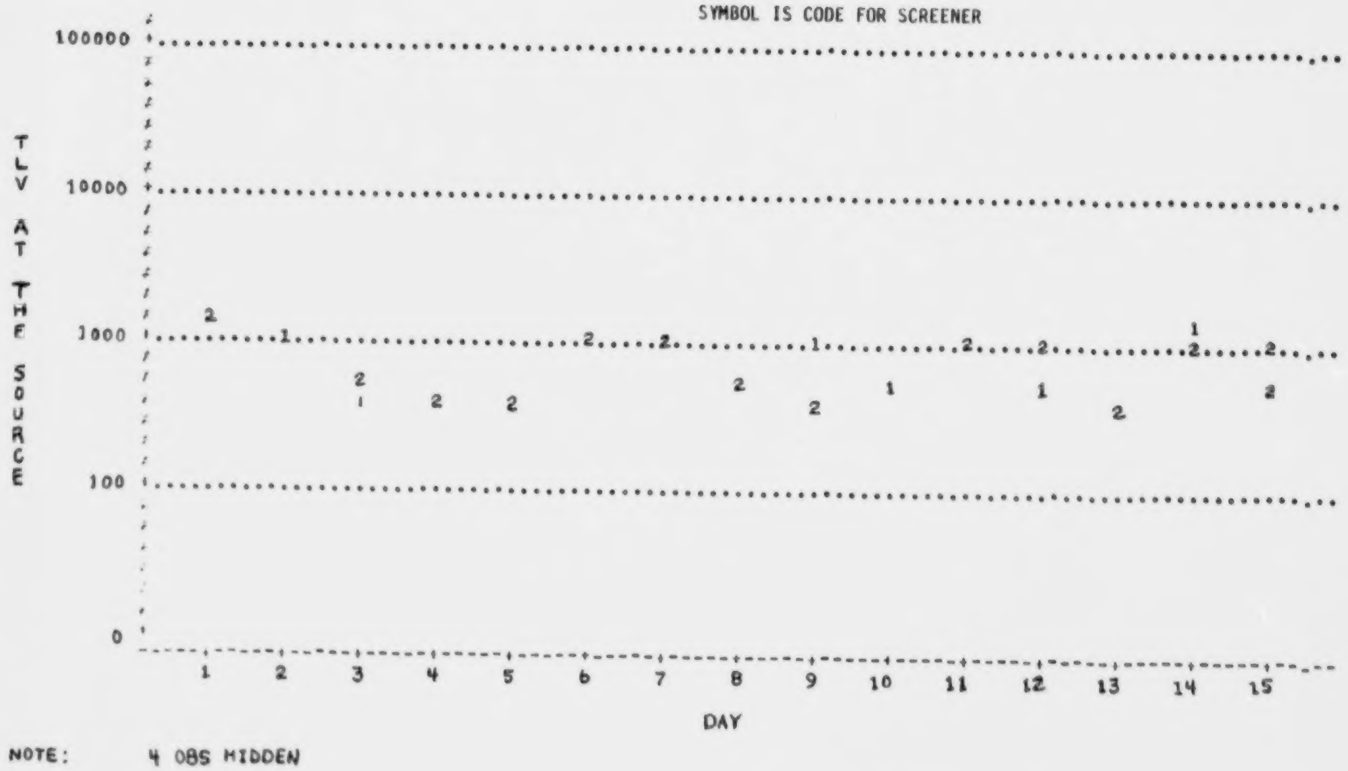
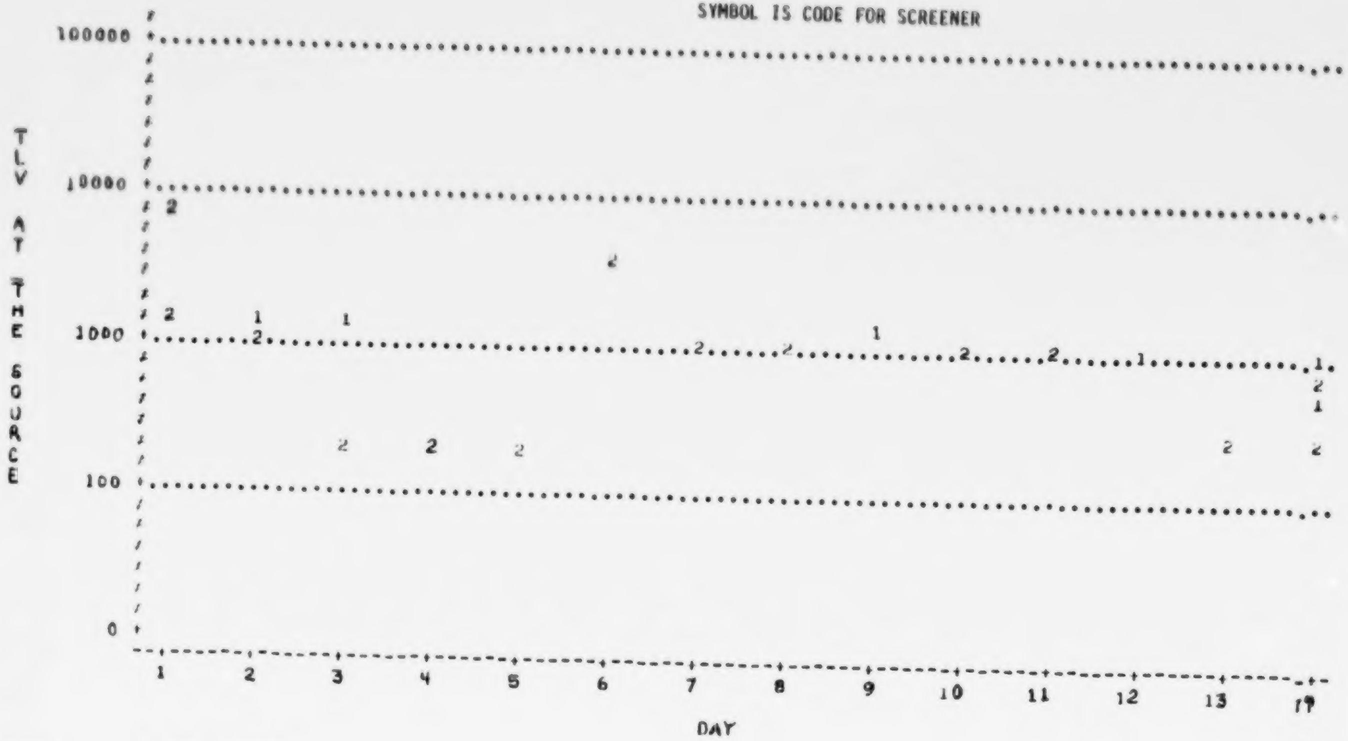


Figure C3-9. TLV Quality Control - Daily Readings at the Source, Refinery F, Pump Seal 75



NOTE: 3 OBS HIDDEN

Figure C3-10. TLV Quality Control - Daily Readings at the Source, Refinery F, Pump Seal 92

by the same team can also be seen. Figures C3-11 and C3-12 represent the paired TLV readings taken 5 cm from the source on the same sources. Note that the magnitude of the concentration is different. The magnitude of the difference between operators is larger, in one case, and about the same in the other case.

The absolute value of the percent difference between operators was calculated and is plotted against the mean value for operators in Figures C3-13 and C3-14 for TLV at the source and TLV at 5 cm, respectively. For TLV at the source, most values had less than 60 percent difference. Again, for TLV at 5 cm, the magnitude of the percent differences is larger.

A variance component analysis was run on both TLV sniffer and OVA-108 data from the reproducibility and repeatability studies on selected devices. The results of this analysis, broken down by device, are given in Tables C3-2 and C3-3 for the TLV and OVA. The pooled standard deviation for all TLV repeat readings at the source (all devices) is 0.50 ln (screening value), yielding a 90 percent repeatability of 117 percent.

The effect of different operators can also be observed in this analysis. Pooling the data from pumps and valves, the standard deviation is 56 percent. Ninety percent reproducibility is then equal to 130 percent. The pooled standard deviation for all OVA (at the source) repeat readings is 30.5 percent producing a repeatability of 85 percent. Note that the repeatability of the OVA instrument appears better than that of the TLV, and that there are less data available to evaluate the OVA.

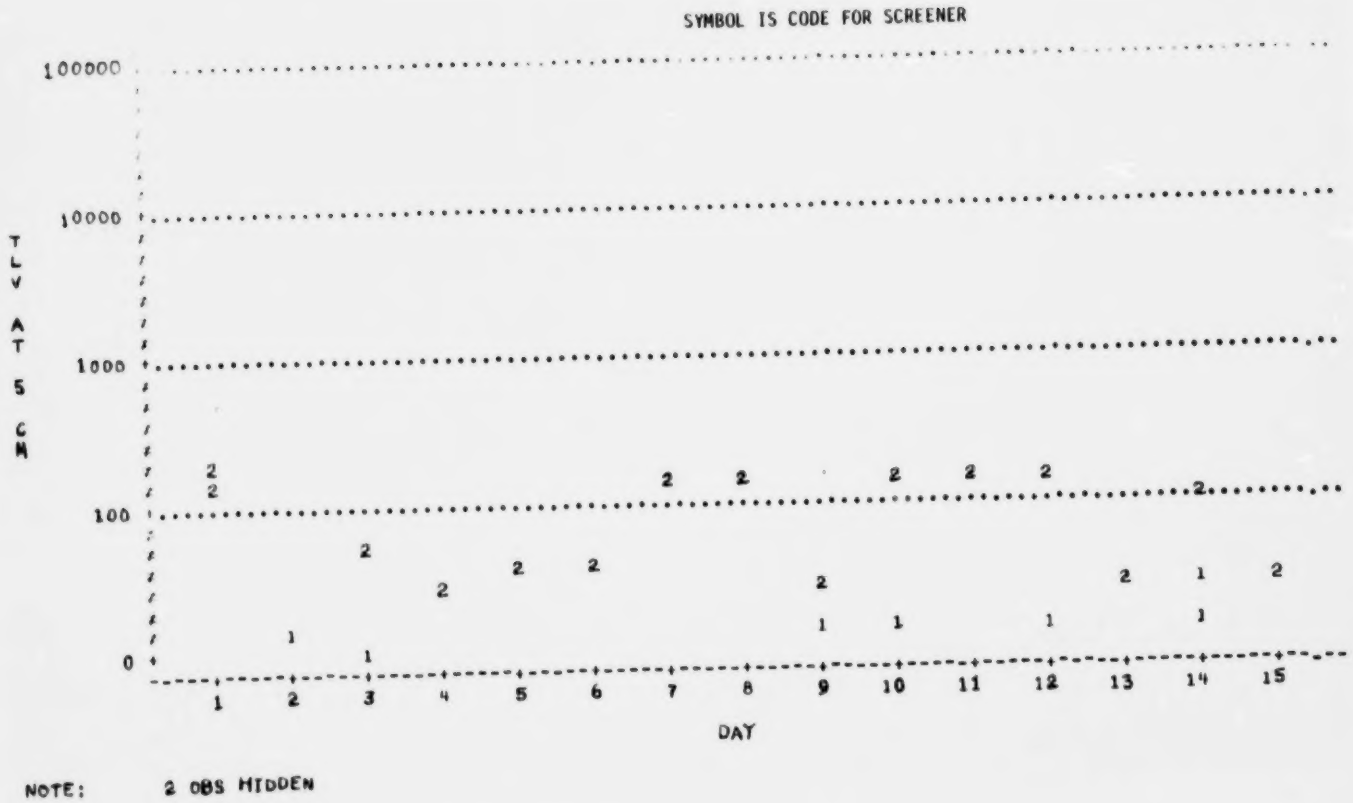


Figure C3-11. TLV Quality Control - Daily Readings - 5 cm from Source, Refinery F, Pump Seal 75

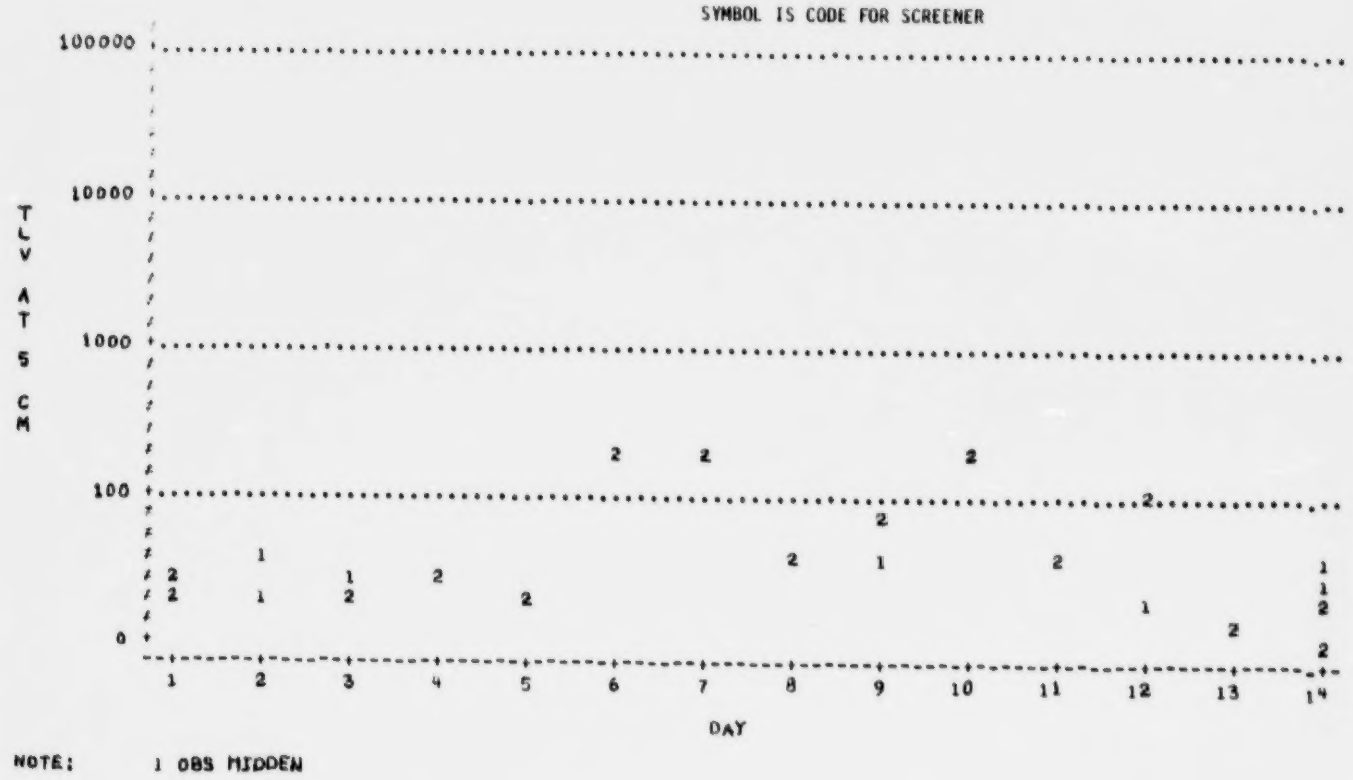


Figure C3-12. TLV Quality Control - Daily Readings 5 cm from Source, Refinery F, Pump Seal 92

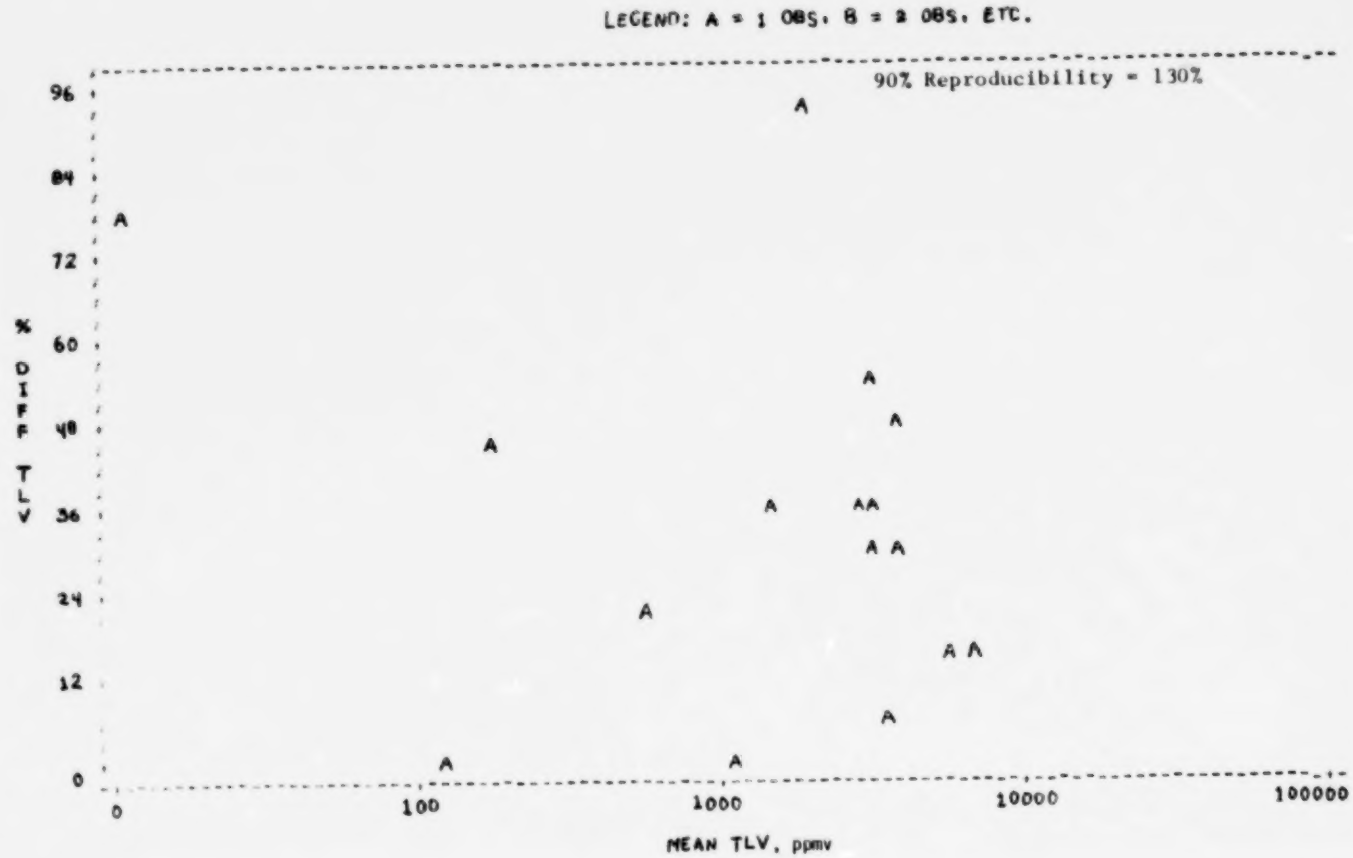


Figure C3-13. Percent Difference in TLV Readings at the Source by Different Screeners

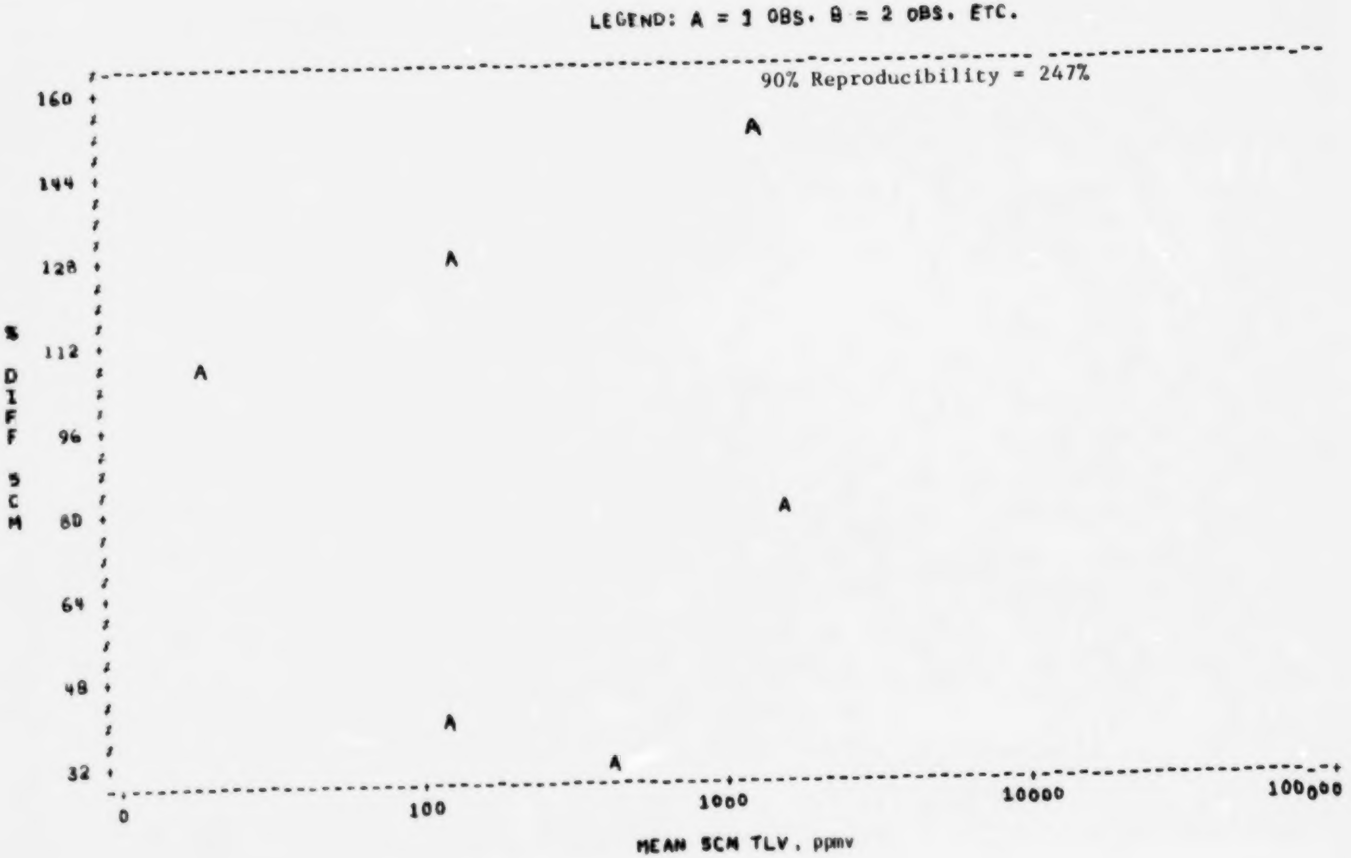


Figure C3-14. Percent Difference in TLV Readings 5 cm from Source by Different Screeners

TABLE C3-2. VARIANCE COMPONENTS FOR TLV MEASURED AT THE SOURCE

Valves - Ln (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	155	2.847	100
INDIVIDUAL VALVES	5	1.384	48.6
DAY	70	1.134	39.8
OPERATOR	39	0.060	2.1
REPEAT	41	0.269	9.5

90% Repeatability = 121%

90% Reproducibility = 134%

Pump Seals - Ln (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	46	0.427	100
INDIVIDUAL PUMPS	1	-0.008	0.0
DAY	27	0.192	44.9
OPERATOR	10	0.068	15.9
REPEAT	8	0.167	39.2

90% Repeatability = 95%

90% Reproducibility - 113%

TABLE C3-3. VARIANCE COMPONENTS FOR OVA MEASURED AT THE SOURCE

Valves Ln (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	23	2.342	100
INDIVIDUAL VALVES	2	1.799	76.8
DAY	15	0.401	17.1
REPEAT	6	0.141	6.1

90% Repeatability = 87%

Pump Seals - Ln (screening value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	15	0.908	100
INDIVIDUAL PUMPS	1	0.359	39.5
DAY	10	0.528	58.2
REPEAT	4	0.021	2.3

90% Repeatability = 36%

Table C3-4 contains the results of the variance components test run on the 5 cm TLV readings. The pooled standard deviation for repeat readings is 0.79 ln (screening value) and the pooled 90 percent repeatability is 184 percent. This high repeatability figure shows the 5 cm method to be more variable than screening at the source. Reproducibility was also calculated by pooling the variance from both devices that described the operator effect. The standard deviation is 1.06 and the percent reproducibility is 246 percent, again much higher than that for screening at the source.

The OVA-108 screening device data from 5 cm was also checked for repeatability (Table C3-5). The pooled standard deviation for repeated readings is 0.28 ln (screening value) and the percent repeatability is 65 percent. The repeatability for the 5 cm OVA readings is slightly better than that for OVA screened at the source (72 percent) but the difference is not statistically significant at the 95 percent test level.

3.3 Relationships Between TLV and OVA Readings and Leak Rates

TLV Versus OVA

The TLV sniffer was the primary screening device used on this program, but the OVA-108 was also available and used for some screening. During the duration of this program, Radian did a study for six San Francisco Bay Area refineries in which the OVA was used for screening. A special study was run to relate TLV and OVA readings. This study is reported here for completeness.

TABLE C3-4. VARIANCE COMPONENTS FOR 5 CM TLV

Valves - Ln (Screening Value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	101	4.613	100
INDIVIDUAL VALVES	4	2.326	50.4
DAY	57	1.327	28.8
OPERATOR	19	0.235	5.1
REPEAT	21	0.725	15.7

90% Repeatability = 198%

90% Reproducibility = 228%

Pump Seals - Ln (Screening Value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	46	1.484	100
INDIVIDUAL PUMPS	1	-0.046	0.0
DAY	27	0.229	0.0
OPERATOR	10	1.124	75.8
REPEAT	8	0.360	24.2

90% Repeatability = 139%

90% Reproducibility = 283%

TABLE C3-5. VARIANCE COMPONENTS FOR 5 CM OVA

Valves - Ln (Screening Value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	23	4.073	100
INDIVIDUAL VALVES	2	2.774	68.1
DAY	15	1.189	29.2
REPEAT	6	0.110	2.7

90% Repeatability = 77%

Pump Seals - Ln (Screening Value)

Variance Source	Degrees of Freedom	Variance Component	Percent
TOTAL	15	0.435	100
INDIVIDUAL PUMPS	1	0.056	12.9
DAY	10	0.351	80.7
REPEAT	4	0.02	6.4

90% Repeatability = 39%

One hundred and twenty valves with TLV screening values from 30 ppmv to 100,000+ were each screened in the following manners:

Device	Calibration Gas	Distance from Source
TLV	hexane	0 cm (at the source)
TLV	hexane	1 cm
OVA	methane	0 cm
OVA	methane	1 cm

For each of the above categories, 120 pairs of screening values were thus available for analysis. The maximum value was recorded following the usual screening procedure. Regression analyses on the logarithm of the maximum screening value were done and nomographs were developed to enable conversion to various types of screening and devices. These nomographs are shown in Figures C3-15 through C3-18. The 90 percent confidence intervals reflect the precision of relationships as determined from the study in the Bay area. When using these nomographs, it is important to note that the instrument is calibrated to the standard gas type listed on the graph.

TLV Versus Leak Rate

Screening values were obtained during the field sampling program when the source was first located and rescreening values were obtained nearer to the time that the source was actually sampled. Correlations and nomographs have been developed to relate the maximum TLV with leak rates. These are reported in Appendix B of this report. A number of summary statistics were evaluated before selecting the maximum reading. Tables C3-6 and C3-7 report simple correlations

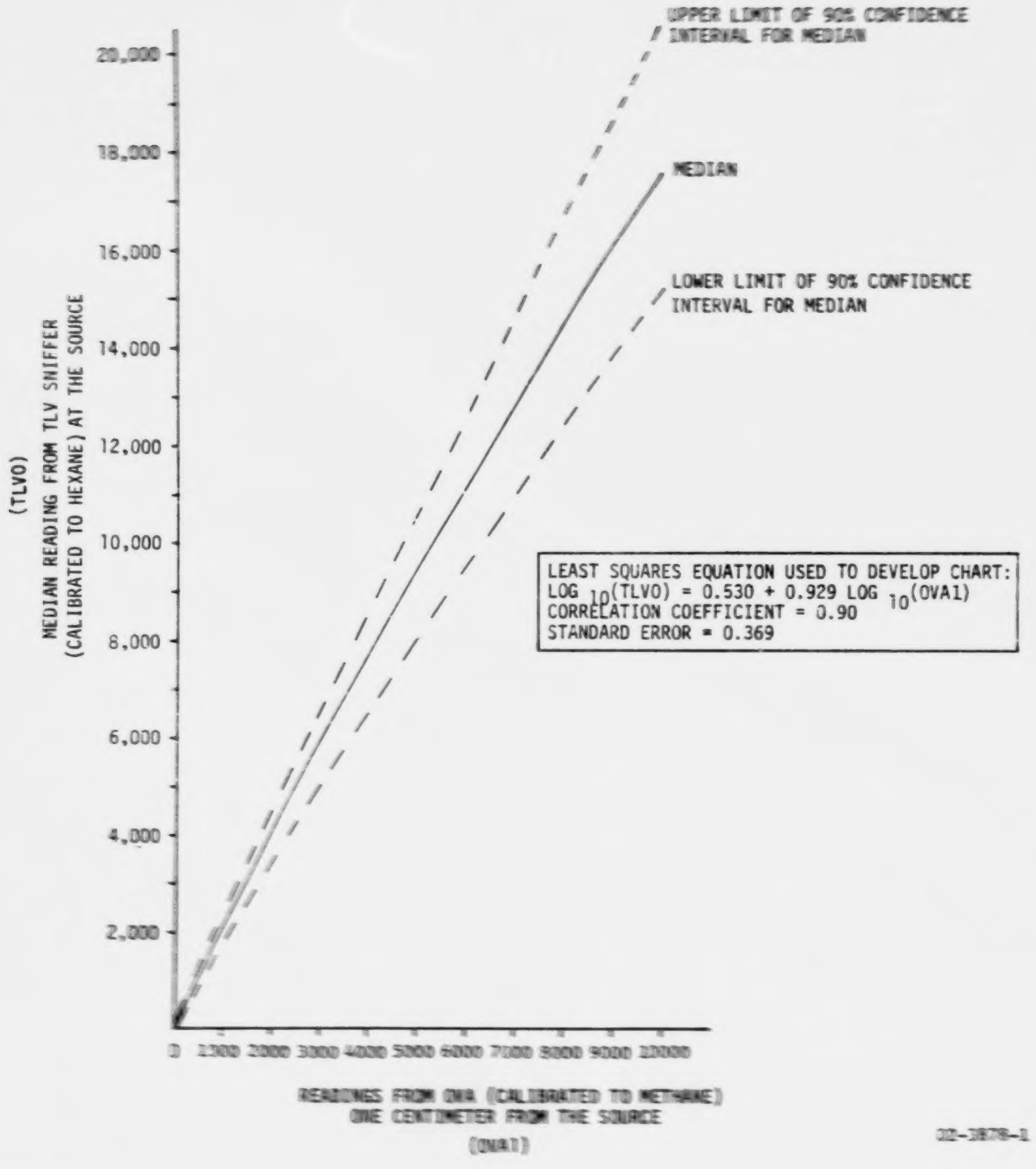


Figure C3-15(a). Nomograph for Relating TLV Sniffer and OVA Readings - Part I.

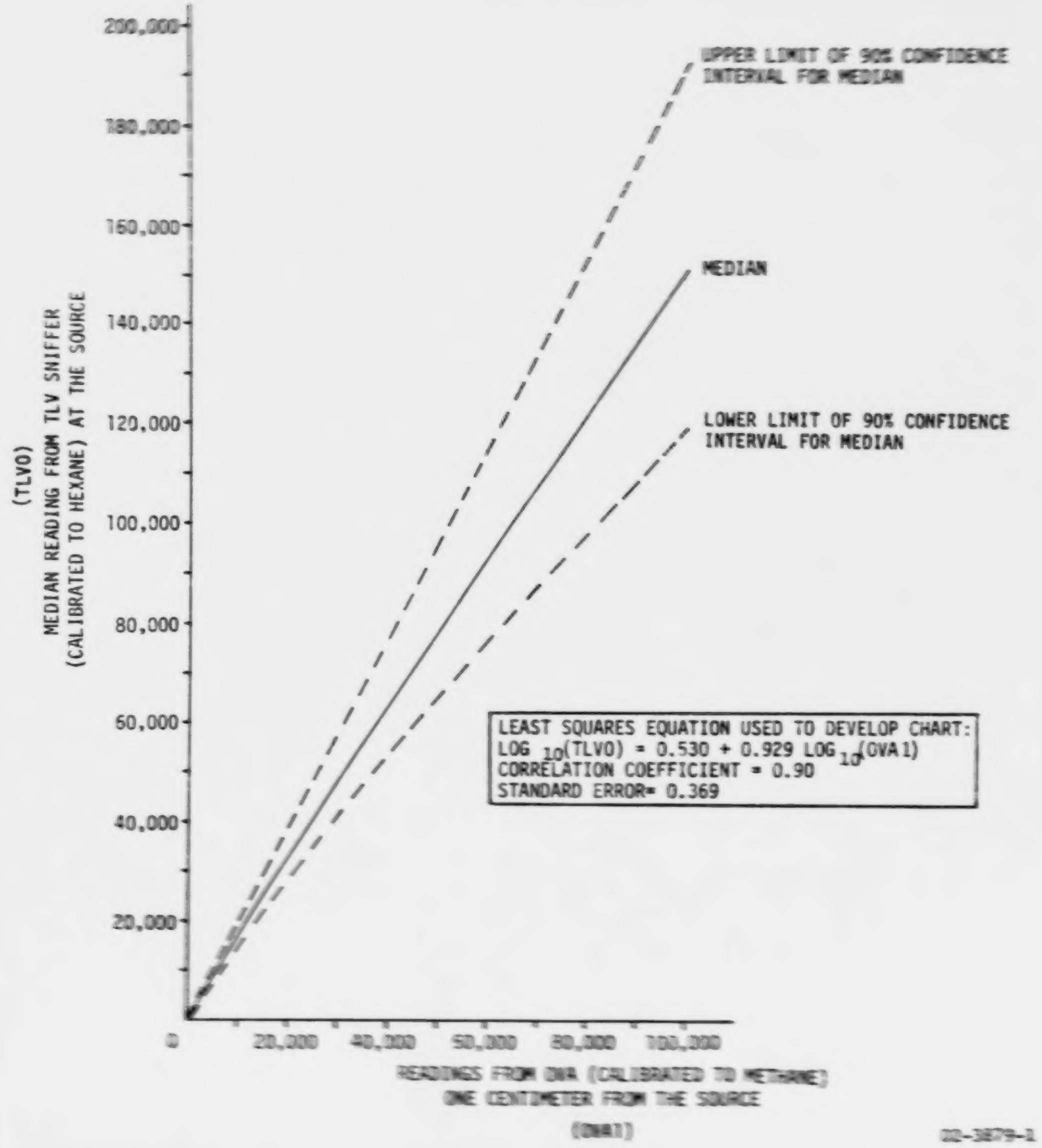


Figure C3-15(b). Nomograph for Relating TLV Sniffer and OVA Readings - Part II.

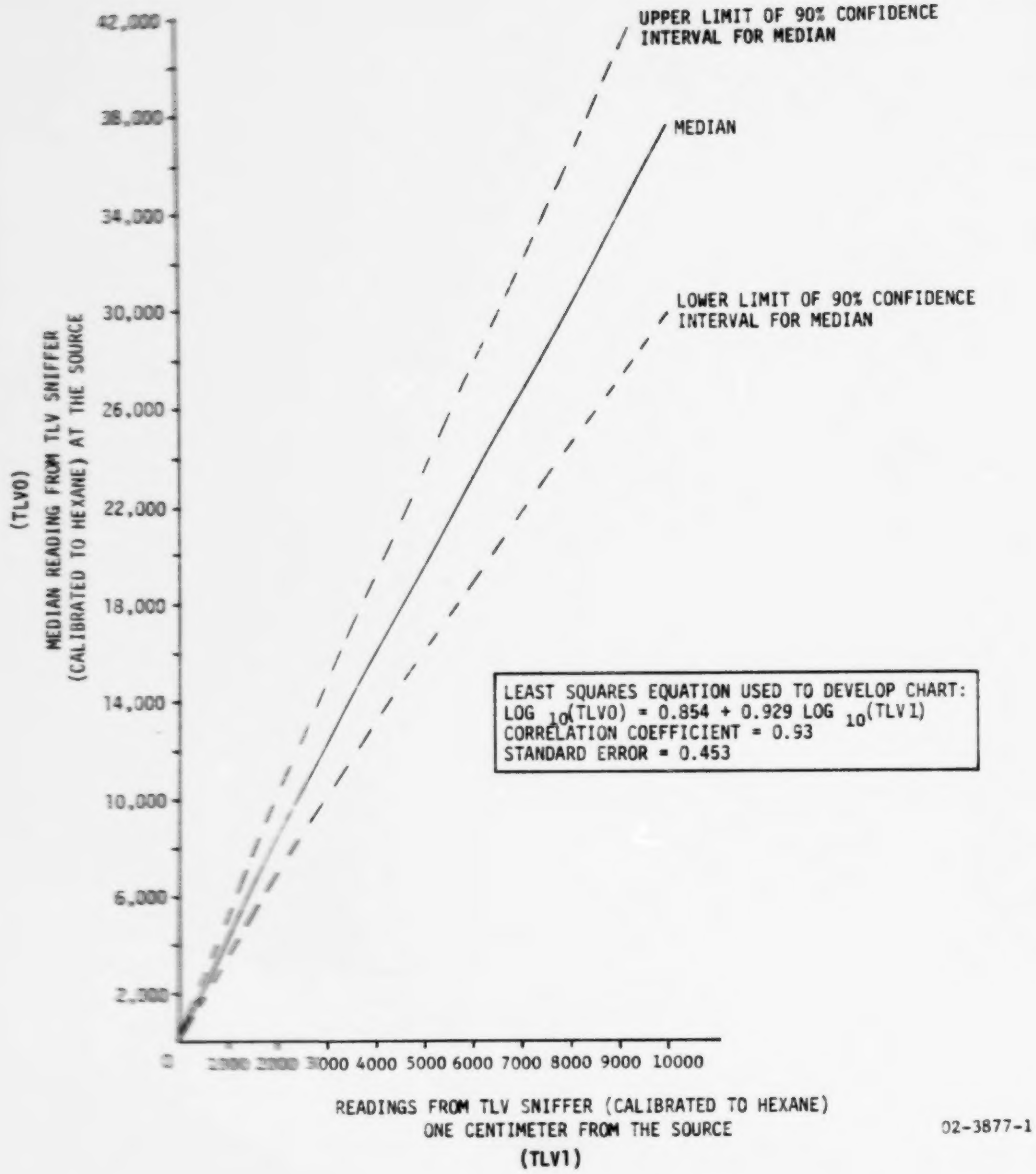
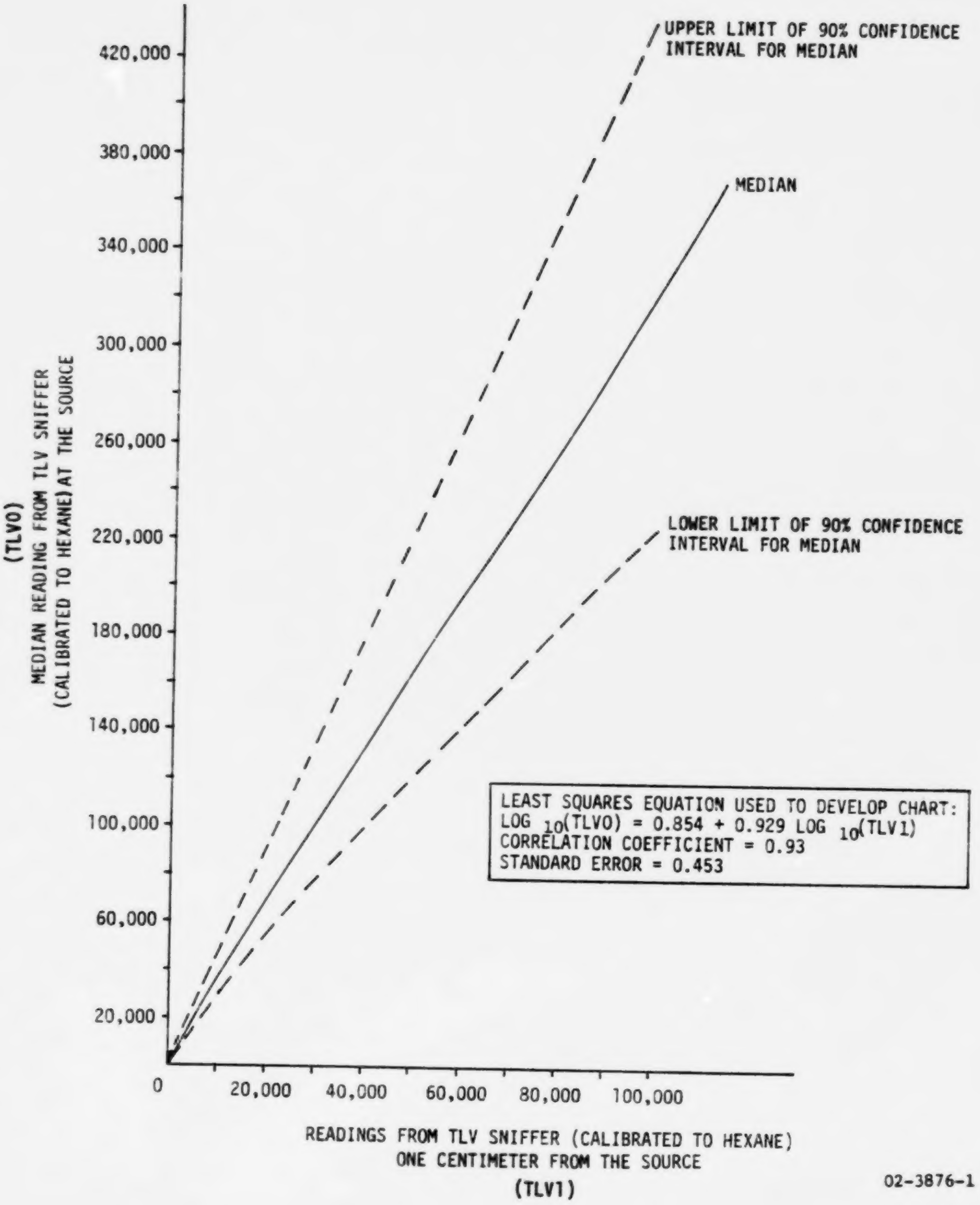


Figure C3-16(a). Nomograph for Relating TLV Sniffer Readings at Zero and One Centimeter - Part I



LEAST SQUARES EQUATION USED TO DEVELOP CHART:
$\log_{10}(TLVO) = 0.854 + 0.929 \log_{10}(TLV1)$
CORRELATION COEFFICIENT = 0.93
STANDARD ERROR = 0.453

Figure C3-16(b). Nomograph for Relating TLV Sniffer Readings at Zero and One Centimeter - Part II

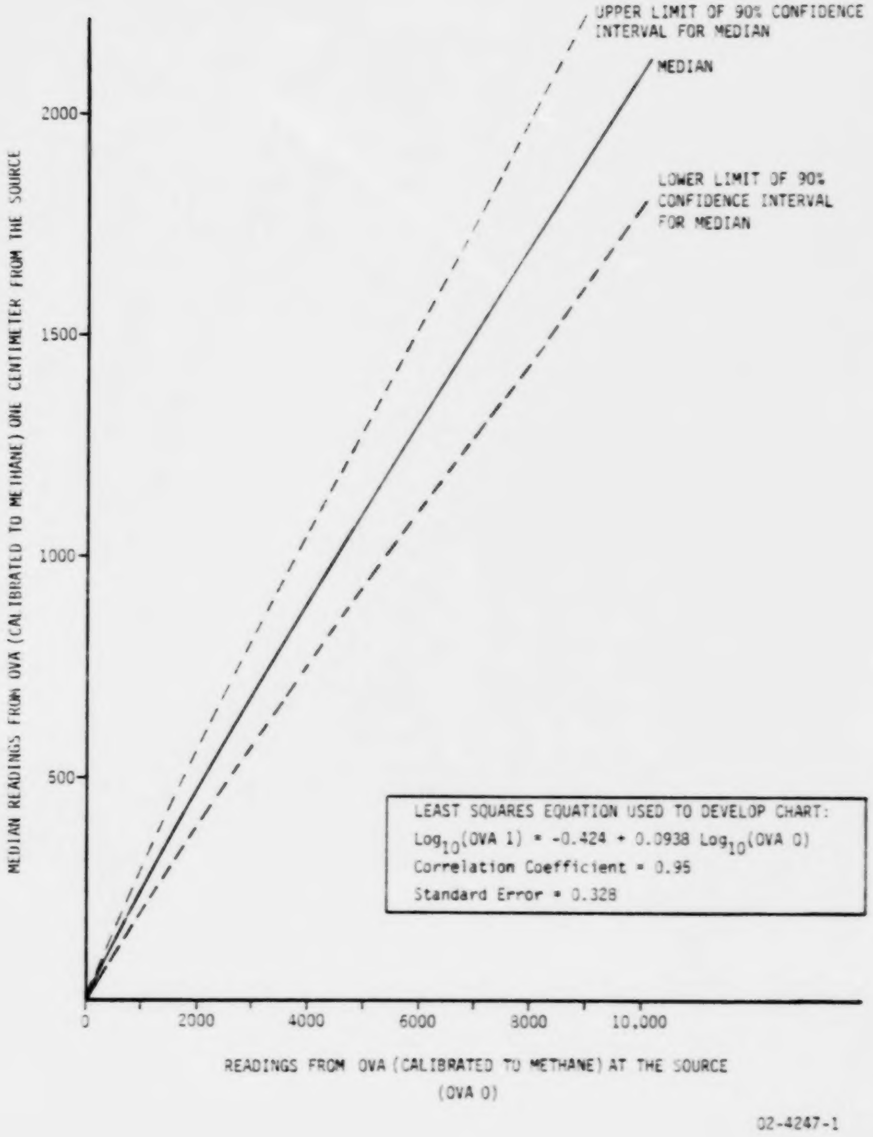


Figure C3-17(a). Nomograph for Relating OVA Readings at Zero and One Centimeter - Part I

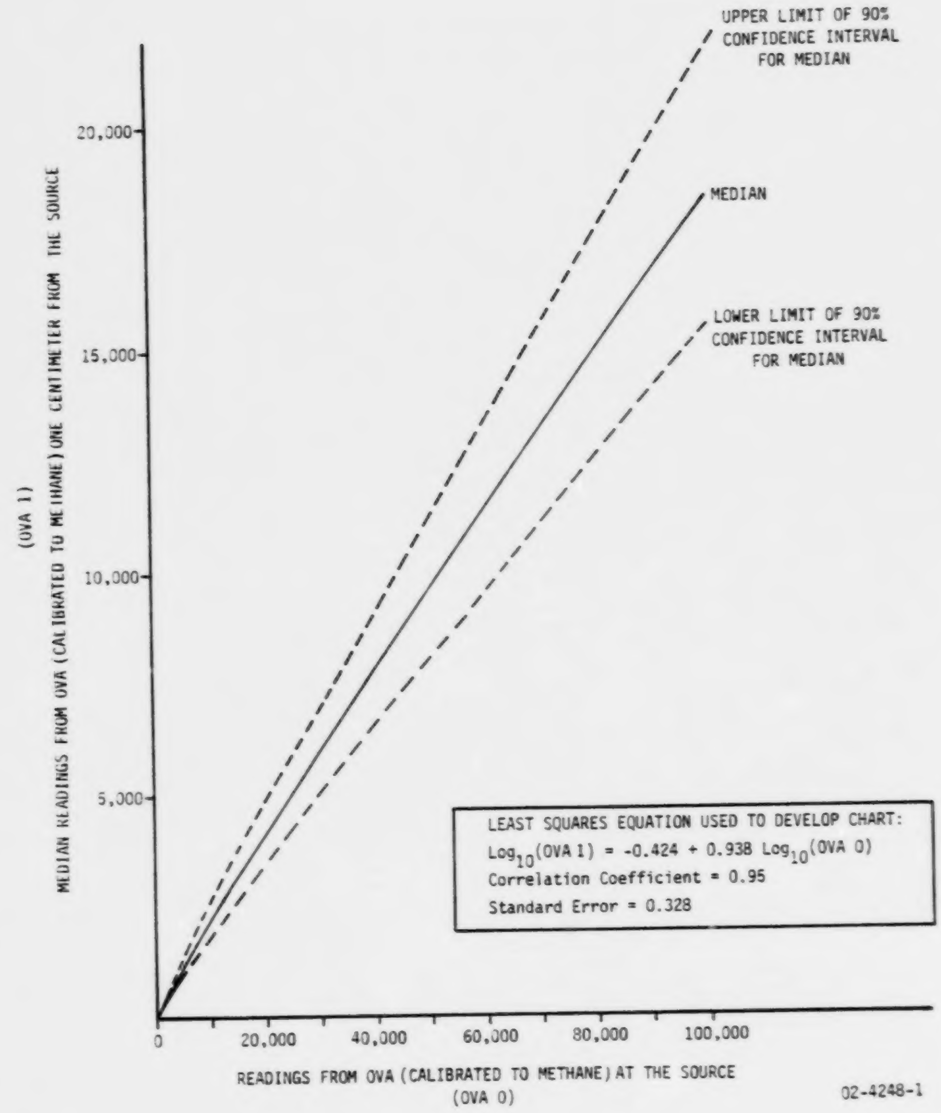


Figure C3-17(b). Nomograph for Relating OVA Readings at Zero and One Centimeter - Part II

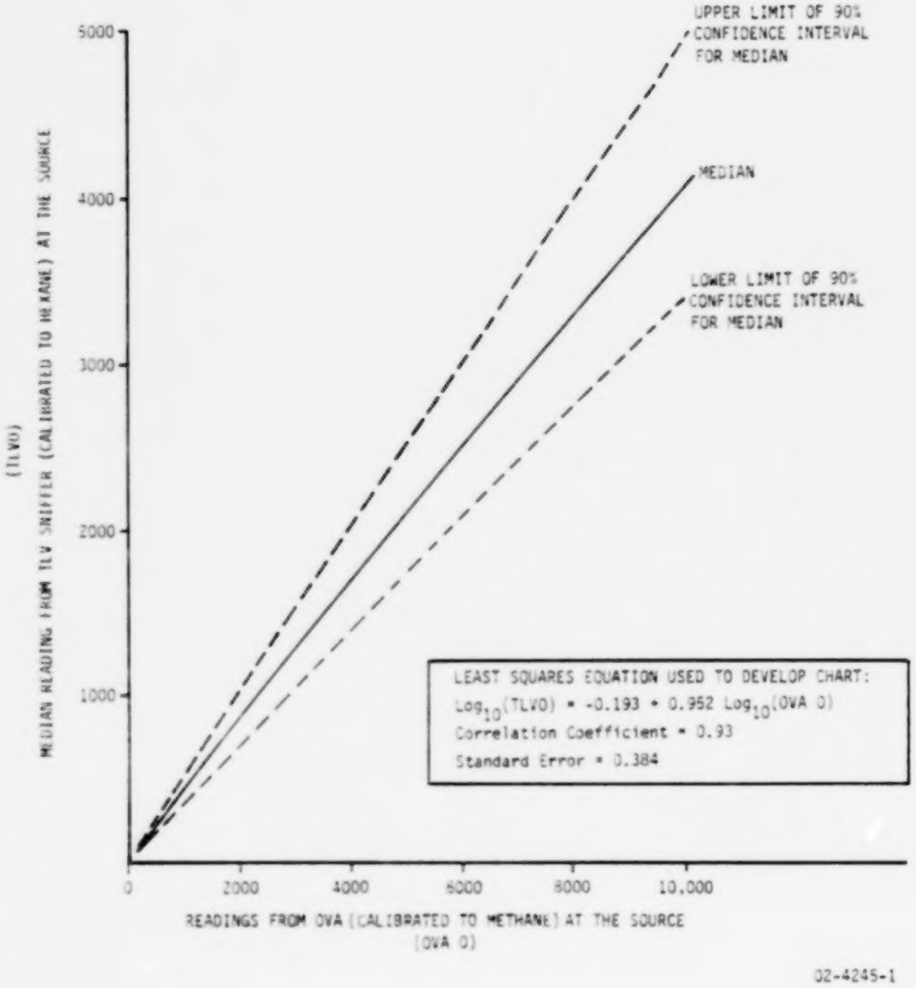


Figure C3-18(a). Nomograph for Relating OVA Readings and TLV Sniffer Readings at the Source - Part I

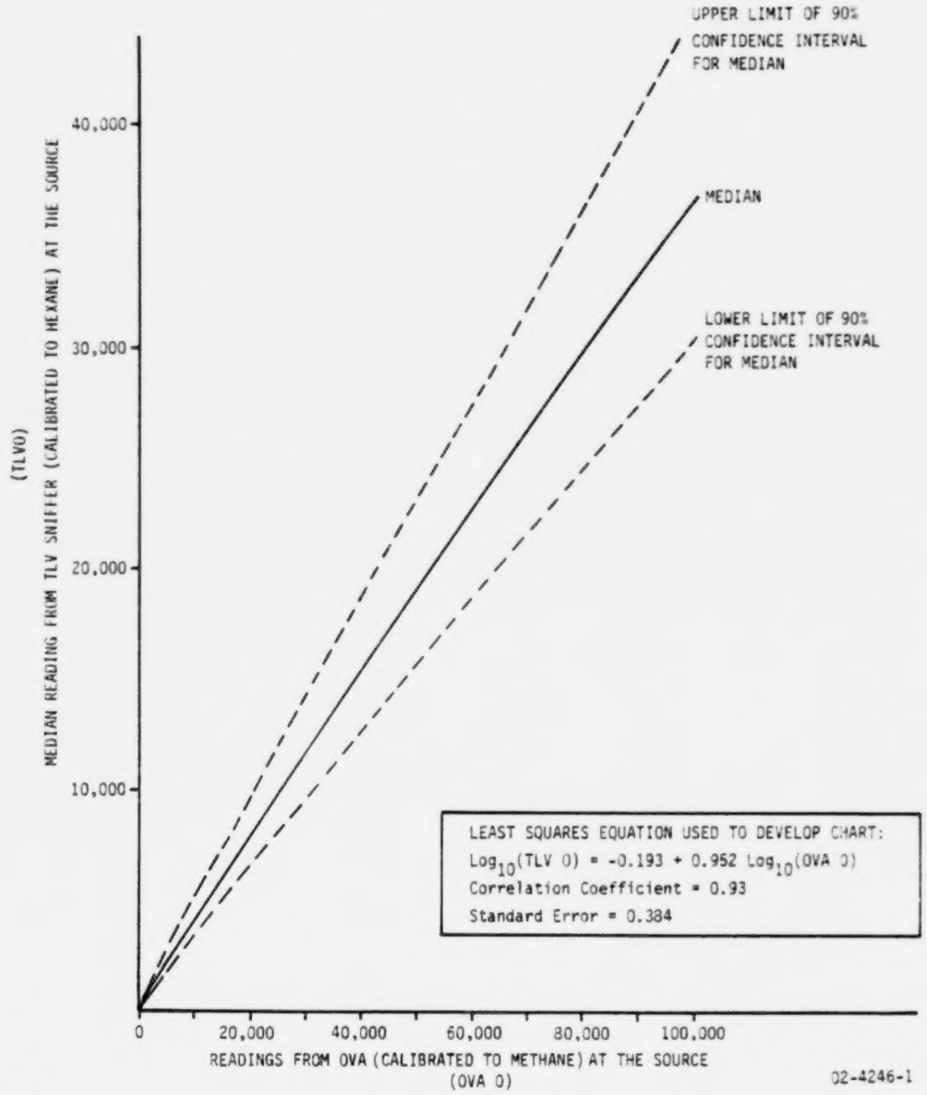


Figure C3-18(b). Nomograph for Relating OVA Readings and TLV Readings at the Source - Part II

TABLE C3-6. CORRELATIONS OF SCREENING VARIABLES AND NONMETHANE LEAK RATES (lb/hr) - VALVES (All Correlations Based on Log of Variable)

VARIABLE	(2) MAX SC	(3) MAX RSC	(4) AVG RSC	(5) 5-CM	(6) N. STM	(7) N. GL
1. Nonmethane Leak	0.628(584)	0.715(260)	0.739(260)	0.685(246)	0.703(251)	0.511(195)
2. Maximum Screening Value	-	0.745	0.748	0.593	0.677	0.434
3. Maximum Rescreening Value		-	0.978	0.804	0.858	0.633
4. Average Rescreening Value			-	0.837	0.890	0.693
5. Avg. of Maximum 5-cm Reading				-	0.733	0.722
6. North Stem Reading					-	0.545
7. North Gland Reading						-

Tabled values are r (m)

r = simple correlation coefficient = $\frac{\Sigma(X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\Sigma(X_i - \overline{X})^2 \; \Sigma(Y_i - \overline{Y})^2}}$ where X and & are the paired variables.

m = number of pairs of data observations used in computing correlation coefficient.

TABLE C3-7. CORRELATIONS OF SCREENING VARIABLES AND NONMETHANE LEAK RATES (lb/hr) - PUMPS (All Correlations Based on Log of Variable)

VARIABLE	(2) MAX SC	(3) MAX RSC	(4) AVG RSC	(5) 5-CM	(6) N. STM
1. Nonmethane Leak	0.636(418)	0.578(169)	0.700(169)	0.731(160)	0.716(164)
2. Maximum Screening Value	-	0.766	0.753	0.618	0.765
3. Maximum Rescreening Value		-	0.987	0.825	0.940
4. Average Rescreening Value			-	0.858	0.958
5. Avg of Maximum 5-CM Reading				-	0.835
6. North Stem Reading					-

Tabled values are r (m)

r = simple correlation coefficient = $\frac{\Sigma(X_i - \overline{X})(Y_i - \overline{Y})}{\sqrt{\Sigma(X_i - \overline{X})^2 \quad (Y_i - \overline{Y})^2}}$ where X and Y are the paired variables.

m = number of pairs of data observations used in computing correlation coefficient.

between leak rates and selected screening statistics (including individual readings) for valves and pump seals. The maximum rescreening value at the source was selected because of its high correlations and simple determination.

3.4 TLV Readings Compared to "Soap Screening"

At one refinery, a short test was made to compare screening of sources using a soap solution with screening using a TLV sniffer. No attempt was made to relate the two types of screening results to leak rates because of the minimal amount of data. The test gives only a qualitative comparison of the two screening techniques. Following the usual screening technique on selected sources, the maximum TLV value was obtained. Then the source was sprayed with either a "snoop" soap solution (relatively thin) or a relatively thick solution made from Ivory liquid soap. Then the "action" or "description" of the soap solution was recorded.

Table C3-8 summarizes these data. The descriptions of the soap solution were grouped into one of four classes as described. The data are plotted in Figure C3-19. As can be seen, the soap solution formed bubbles for all screening values greater than 1,000 ppm except for the vertical sources and one other valve.

TABLE C3-8. COMPARISON OF TLV SNIFFER AND SOAP SPRAY SOLUTION

Source Type	Maximum TLV Reading (ppmv)	Description of Soap Spray Application	Soap Leak rate Class	Horizontal (H) Vertical (V)	Snoop Soap (S) Ivory Soap (I)
Compressor Seal	11,000	1" Bubble in 2 seconds	2	H	S
Pump Seal	6,000	No Bubbles detected	1	V	S
Valve	260	Slight Bubble formation barely detectible	2	H	S
Valve	3,400	Very slight bubbles barely detectible	1	H	S
Valve	10,000	rapidly formed 1/8" bubbles	3	H	S
Valve	40,000	rapidly formed 1/4" bubbles - sudsing	3	H	S
Valve	100k+	rapid 1/2" bubbles - spitting solution	4	H	I
Valve	20,000	no bubbles	1	V	I
Valve	100k+	rapid bubbles - spitting	4	H	I
Valve	100k+	rapid bubbles - spitting	4	H	I
Valve	10,000	rapid 1/2" bubbles	3	H	I
Valve	2,300	no bubbles	1	V	I
Valve	14,000	no bubbles	1	H	I
Valve	100k+	rapid large bubbles - clustering	4	H	I
Valve	80	no bubbles	1	V	I
Valve	100k+	rapid 1/4" bubbles	3	H	I

Soap Leak Rate Class
1. no bubbles - very slight
2. slight bubbles
3. rapid bubbles
4. rapid, spitting, clustering

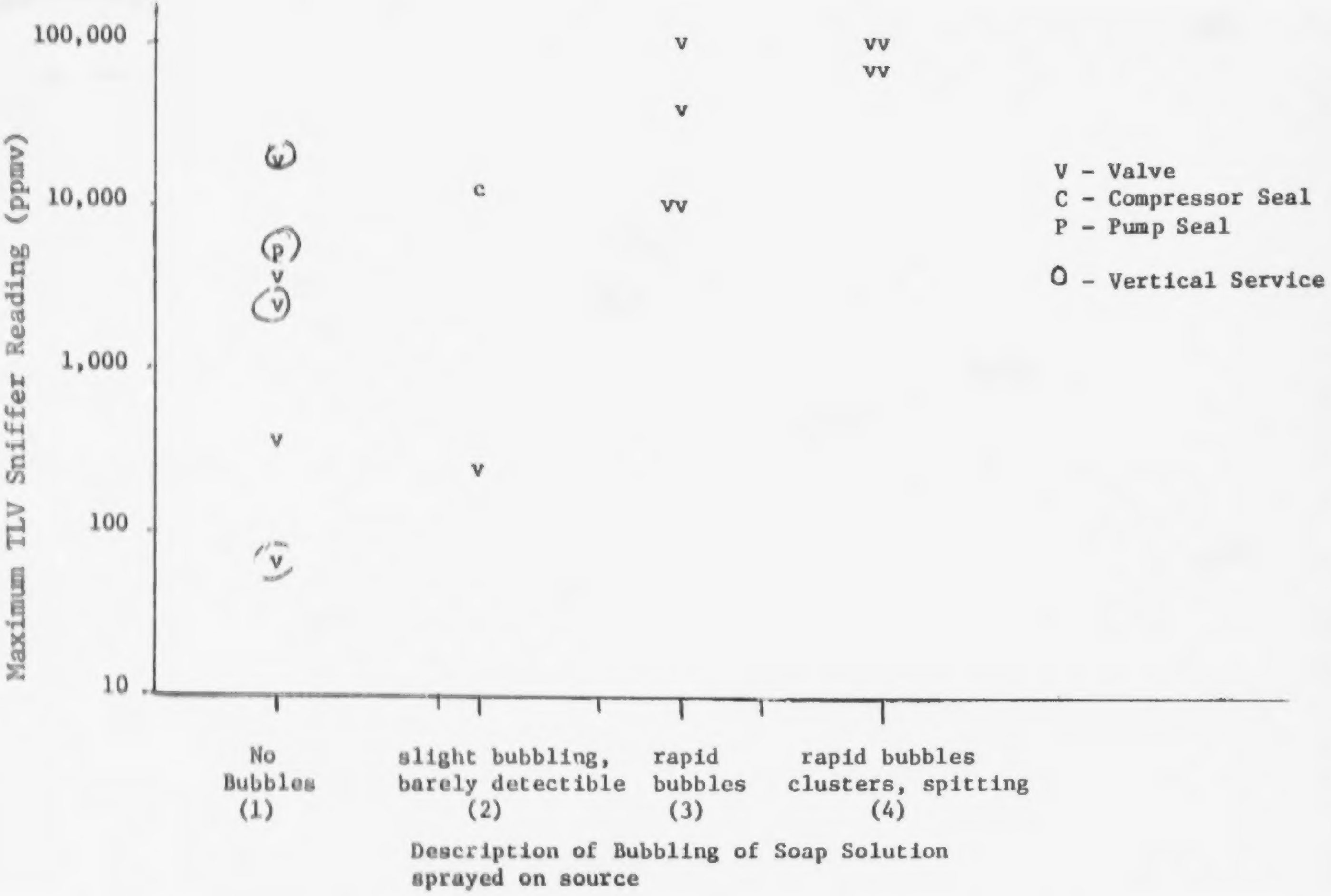


Figure C3-19. Relationship of TLV Sniffer Reading and Bubbling from Soap Solution

4.0 QUALITY CONTROL FOR NONBAGGABLE SOURCES

Quality control for nonbaggable sources involved an evaluation of the accuracy and repeatability of all analytical procedures. Sampling procedures usually did not lend themselves to accuracy evaluations although day-to-day variations give an upper bound on sampling repeatability.

The procedures discussed in this section include an evaluation of the quality control for analytical methods used to measure emissions from cooling towers, wastewater treating units, and process stacks. The specific sampling and analysis procedures, including calibration procedures, are discussed in Appendix A, "Sampling Methodology."

4.1 TOC Analysis for Cooling Tower Evaluation

Total organic carbon (TOC) assays were done during this program with a Dohrmann DC52D TOC analyzer. This instrument oxidizes organics to carbon dioxide and then reduces the carbon dioxide to methane. The methane is measured with a flame-ionization detector.

The instrument was zeroed using a "zero carbon water standard" which was especially prepared for this analysis by Radian. The water is deionized, filtered and distilled from potassium permanganate under helium with a high reflux. This has been proven superior to commercial standards. The standard for the analysis is 180 ppm carbon in water available from Dorhmann. The 180 ppm standard was analyzed on a regular basis during the time that wastewater samples were being analyzed in the field and in Radian's laboratory in Austin. Figure C4-1 shows the results of these 47 analyses. The following results summarize these analyses:

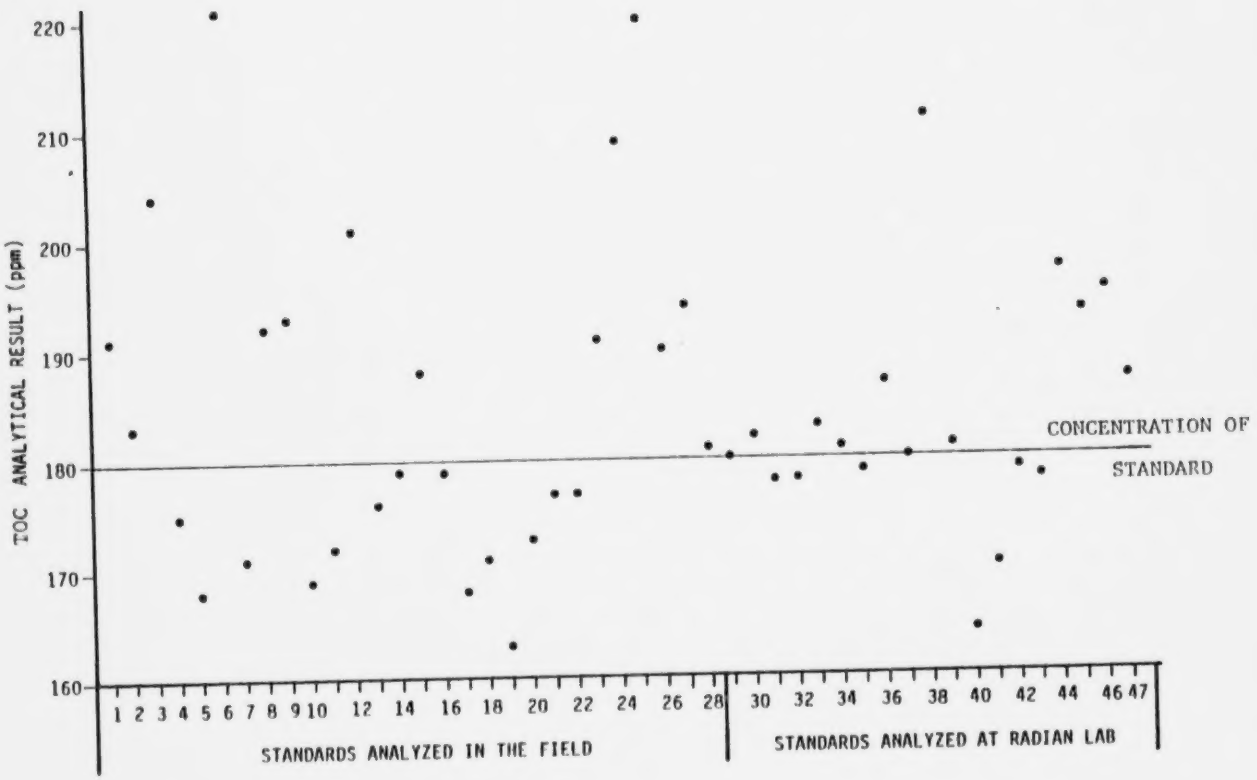


FIGURE C4-1. TOC Standards Analysis

Average: 184.2 ppm
Standard Deviation: 13.54 ppm (7.4% of mean)
95 Percent Confidence interval for average: (180 ppm, 188 ppm)

While these standard analyses do not indicate any bias in the method, the variability of the standard analyses indicates that repeat analyses of samples can differ by as much as 21 percent (95 percent repeatability) at high TOC levels.

Figure C4-2 shows the results of the blank water analysis done during the analyses of samples at Radian's laboratory. These analyses averaged about 1.1 ppm with a standard deviation of 1.8 ppm or 155 percent. These results indicate that interference and repeatability problems could occur in samples at low TOC levels ($<$ 10 ppm).

The difference between the TOC concentrations at the inlet and outlet of the cooling tower (ΔTOC) is the most important statistic in calculating cooling tower emissions. The repeatability of the TOC analysis can be evaluated by comparing replicate determinations of ΔTOC on the same sample. Figure C4-3 shows a plot of the difference between two determinations of ΔTOC on samples from seven cooling towers.

The average difference for these 48 comparisons was 4.2 ppm. By averaging the squared differences, the standard deviation for the method can be estimated. For these samples, the standard deviation is also 4.2 ppm. Note that the average ΔTOC's for these towers range from - 2.1 ppm to 12.2 ppm. Six of the seven towers have an average ΔTOC of less than the standard deviation of repeat analysis. From the plot in Figure C4-3, the repeatability of the analysis appears erratic; for

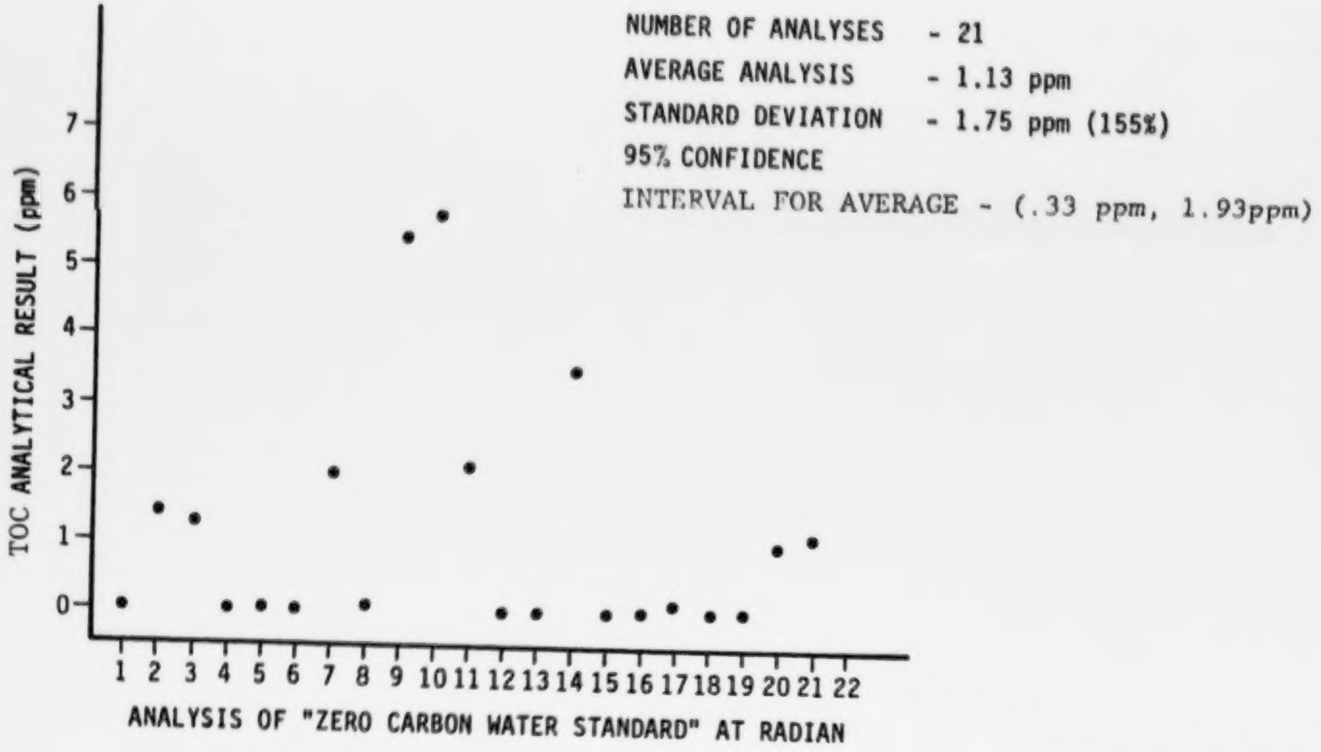


FIGURE C4-2. TOC BLANK ANALYSIS

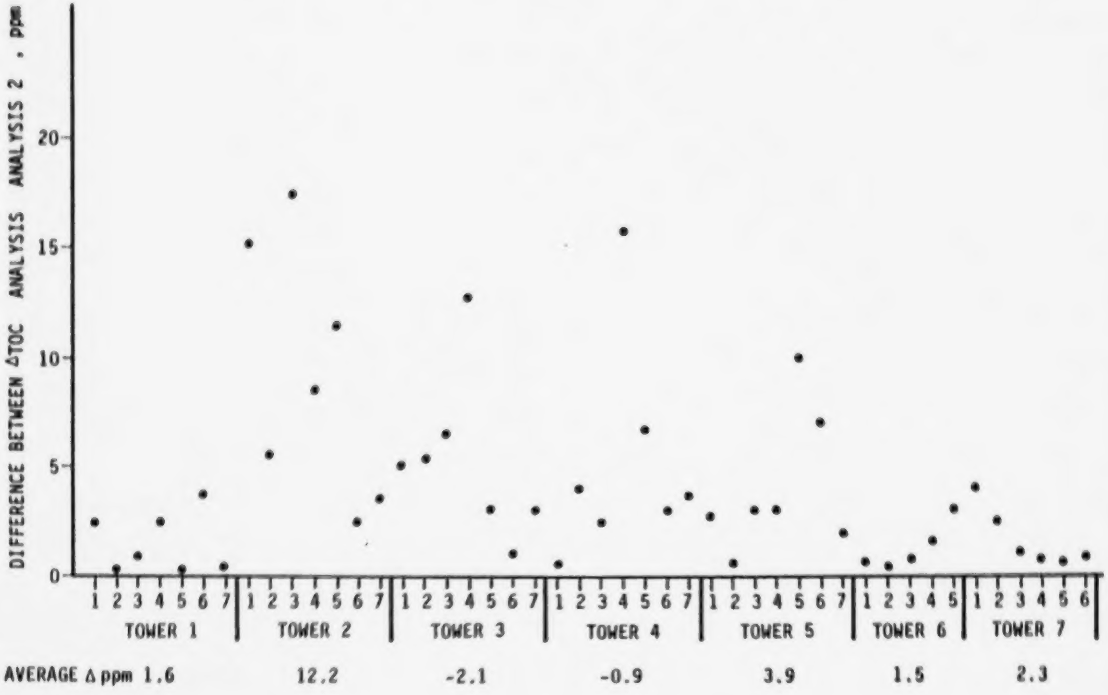


FIGURE C4-3. TOC REPEAT ANALYSIS

three of the towers, all differences are less than 5 ppm. This erratic pattern may be due to the potential interferences discussed above.

Based on a standard deviation of 4.2 ppm, five sets of analyses would be required to consistently measure a significant change of 4.0 ppm in a sample. Two sets of measurements averaged would have some negative changes unless the true change in the sample set were greater than 6.0 ppm. Sampling and time variations would introduce additional variability that would further hinder the measurement of emission using the TOC method.

The magnitude of the sampling and TOC analytical variations caused some problems in quantifying the low levels of emissions from the towers. The standard deviation of day-to-day sampling results using the TOC analyses was close to the analytical standard deviations when replicate samples are averaged. It appears, then, that most of the variation in the TOC analytical data is due to the variability of the analytical technique.

Analytical results obtained by the purge method (discussed below) were much more precise than those obtained from TOC analyses.

4.2 Purge Analysis Method

The purge analysis method was used to measure purgeable volatile organics for both cooling tower and wastewater samples. For cooling tower samples, a 75 ml aliquot was used. For wastewater aqueous phase sample, a 10 ml sample was used. For wastewater oil phase samples, a 10 μl aliquot of oil in

10 ml of water was used. A complete description of the analytical method is given in Appendix A.

Blind standards were run to determine the percent recovery obtainable by the purge method. Figure C4-4 graphs the results of the standards. Almost all the results appear to fall within two standard deviations of the mean percent recovery of 85.4 percent. A 95 percent confidence interval for the average recovery based on the data in Figure C4-4 is 85.4 ± 7.0 percent or 78 to 93 percent, so the recovery appears to average less than 100 percent.

Multiple analyses of samples were performed on both cooling tower and wastewater samples. Figure C4-5 shows the results of the multiple analyses of samples from cooling towers. The maximum percent difference of the multiple samples is plotted against the mean sample concentration. The mean percent difference for all sets of samples was 137 percent with a standard deviation of 80 percent. This yields a 95 percent repeatability of 221 percent.

Figure C4-6 shows the same percent difference versus mean concentration for oil-layer wastewater samples. The mean percent difference for all samples was 7.0 with a standard deviation of 2.7 percent. The 95 percent repeatability then becomes 7.4 percent.

4.3 Gravimetric Method for Evaluating VOC Content of Oil

Total volatile hydrocarbons were also measured in the wastewater oil samples by gravimetric determination. Samples were weighed, then stirred for eight hours. A complete description of the analysis method is given in Appendix A.

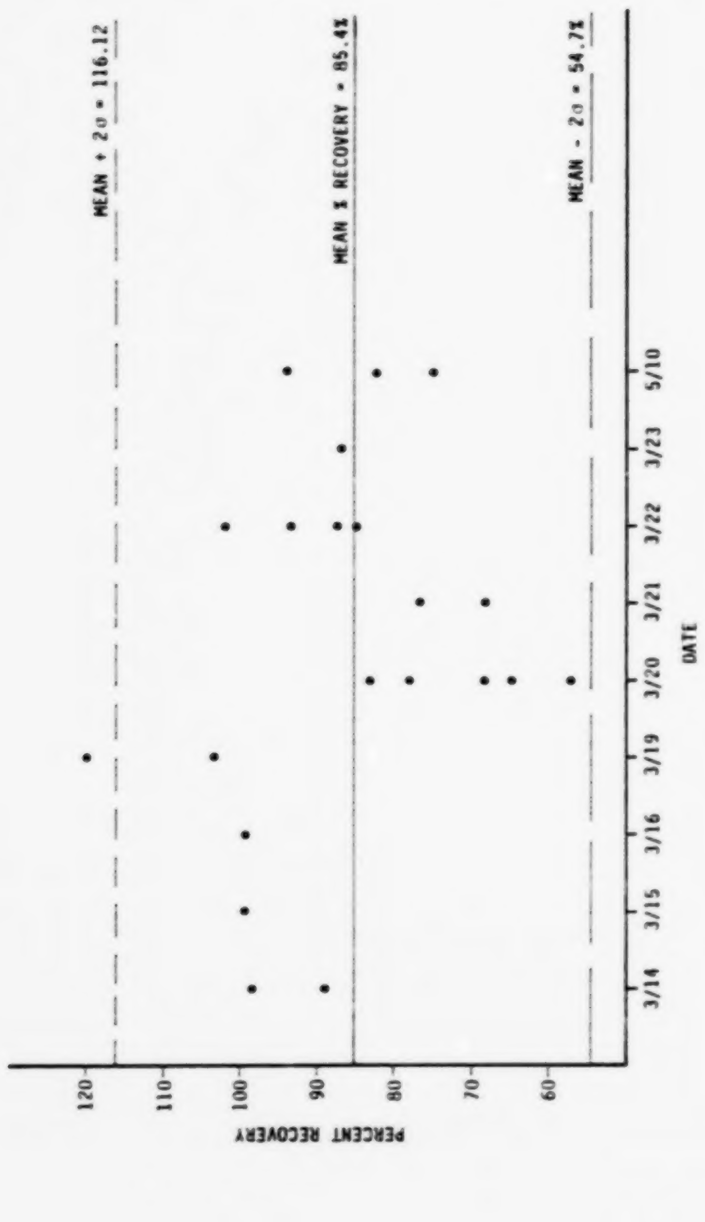


Figure C4-4. Purge Standards Analysis

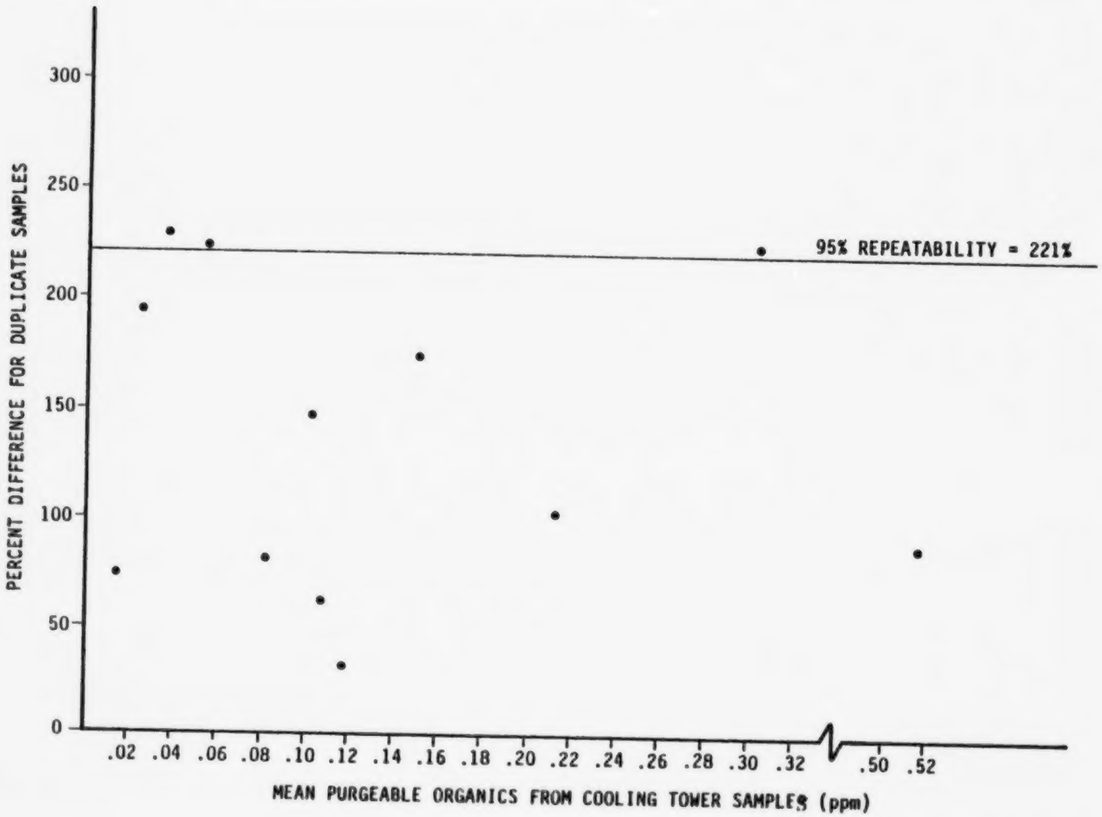


Figure C4-5. Repeatability of Purge Analysis - Cooling Tower Water Samples

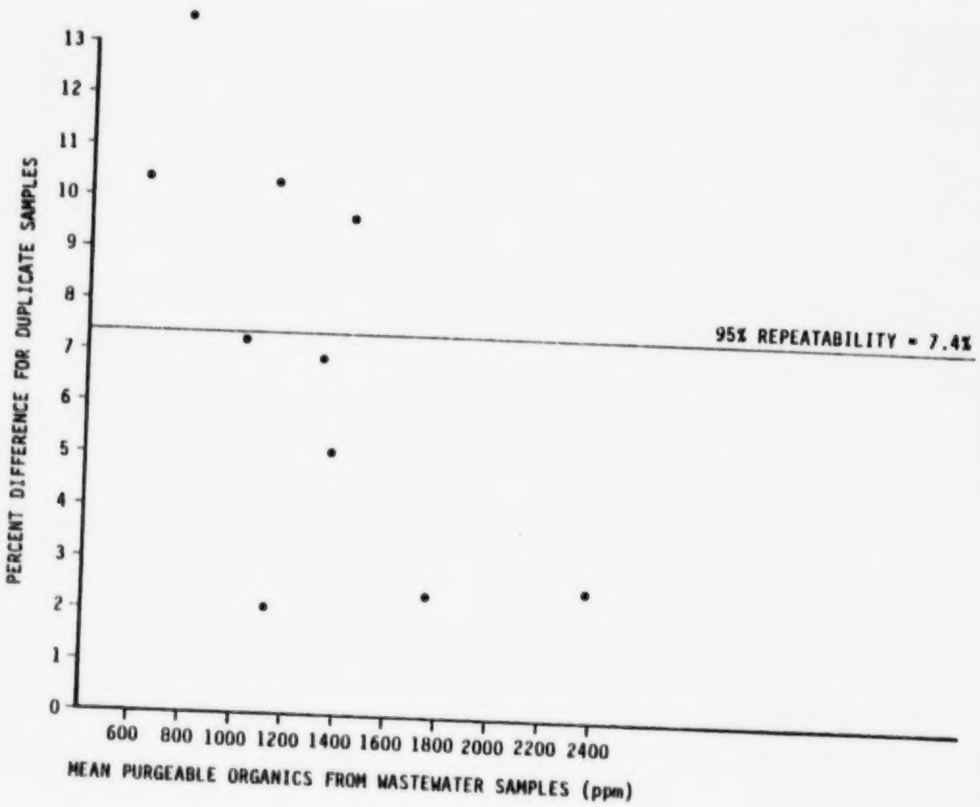


Figure C4-6. Repeatability of Purge Analysis - Wastewater Samples

Standard mixtures of base oil and isooctane were prepared and analyzed. Figures C4-7 and C4-8 show the results of these standards. The average percent recovery was 98.3 percent and recoveries within two standard deviations of the mean range between 90 and 107 percent. A 95 percent confidence interval for the average recovery is 98.3 ± 3.5 percent, so there is no evidence that the true mean recovery is different than 100 percent.

Duplicate gravimetric determinations were also performed on wastewater samples. Figure C4-9 shows the percent difference between duplicates plotted against the mean concentration. Note that there are four very high points on the graphs with percent differences ranging from 68 to 300 percent. This would seem to indicate that for sample concentrations below 0.5 ppm the method is unreliable. The mean percent difference for samples greater than 0.5 ppm concentration is 11.8 percent. The pooled standard deviation for this group is 9.5 percent producing a 95 percent repeatability of 26.4 percent.

4.4 Sampling and Analysis of Process Stack Emissions

The major emphasis on quality control for stack sampling is on strict calibration of metering and temperature control devices, leak testing, and laboratory standard analysis.

Of primary concern in obtaining samples from process stacks and ducts is that the sampling equipment is in proper operating condition prior to and during sampling. In order to achieve this, equipment was inspected and cleaned thoroughly, monitoring devices checked and calibrated, and volume

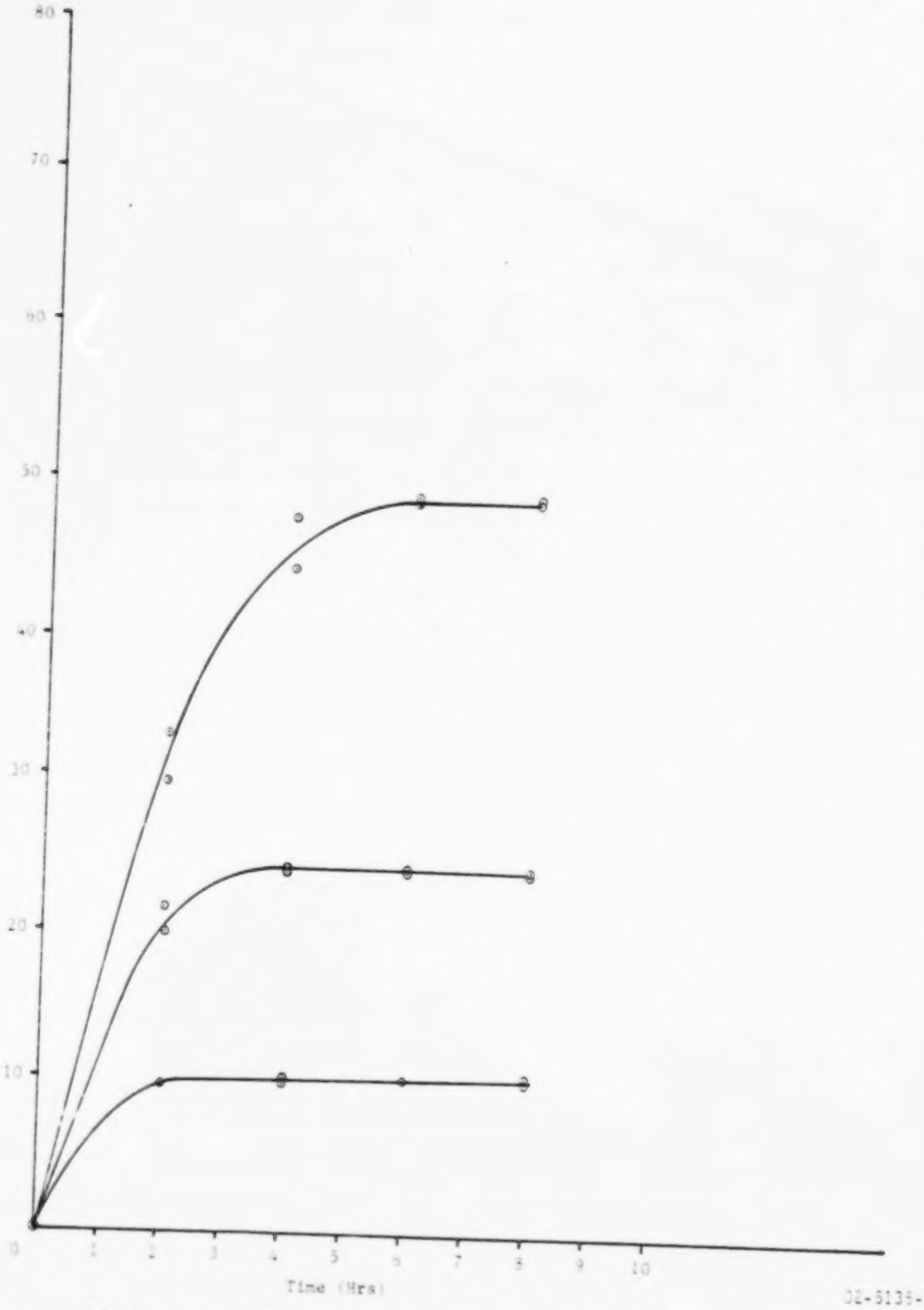


Figure C4-7. Gravimetric Standards Volatile Loss During Eight Hours

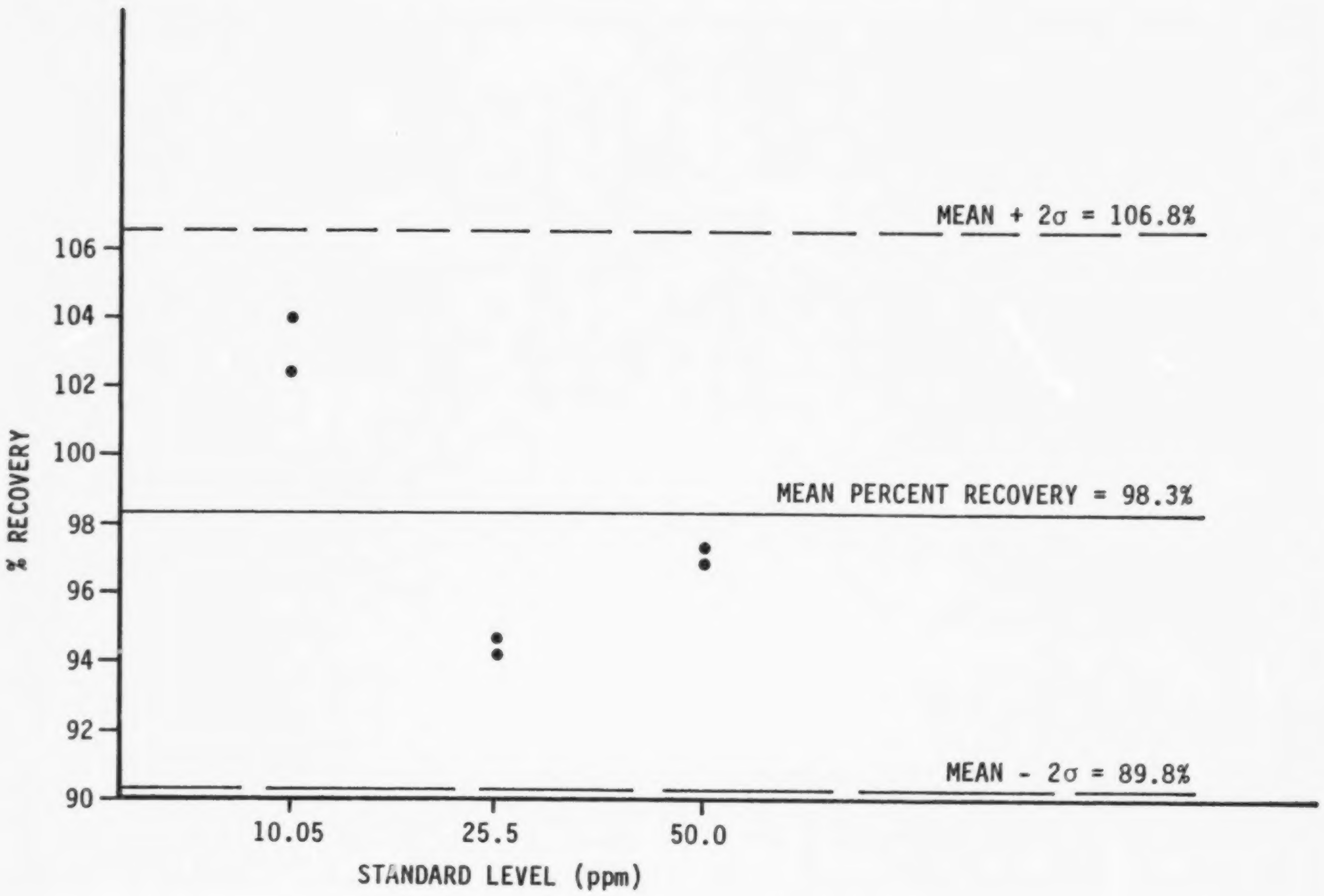


Figure C4-8. Standards for Gravimetric Determination

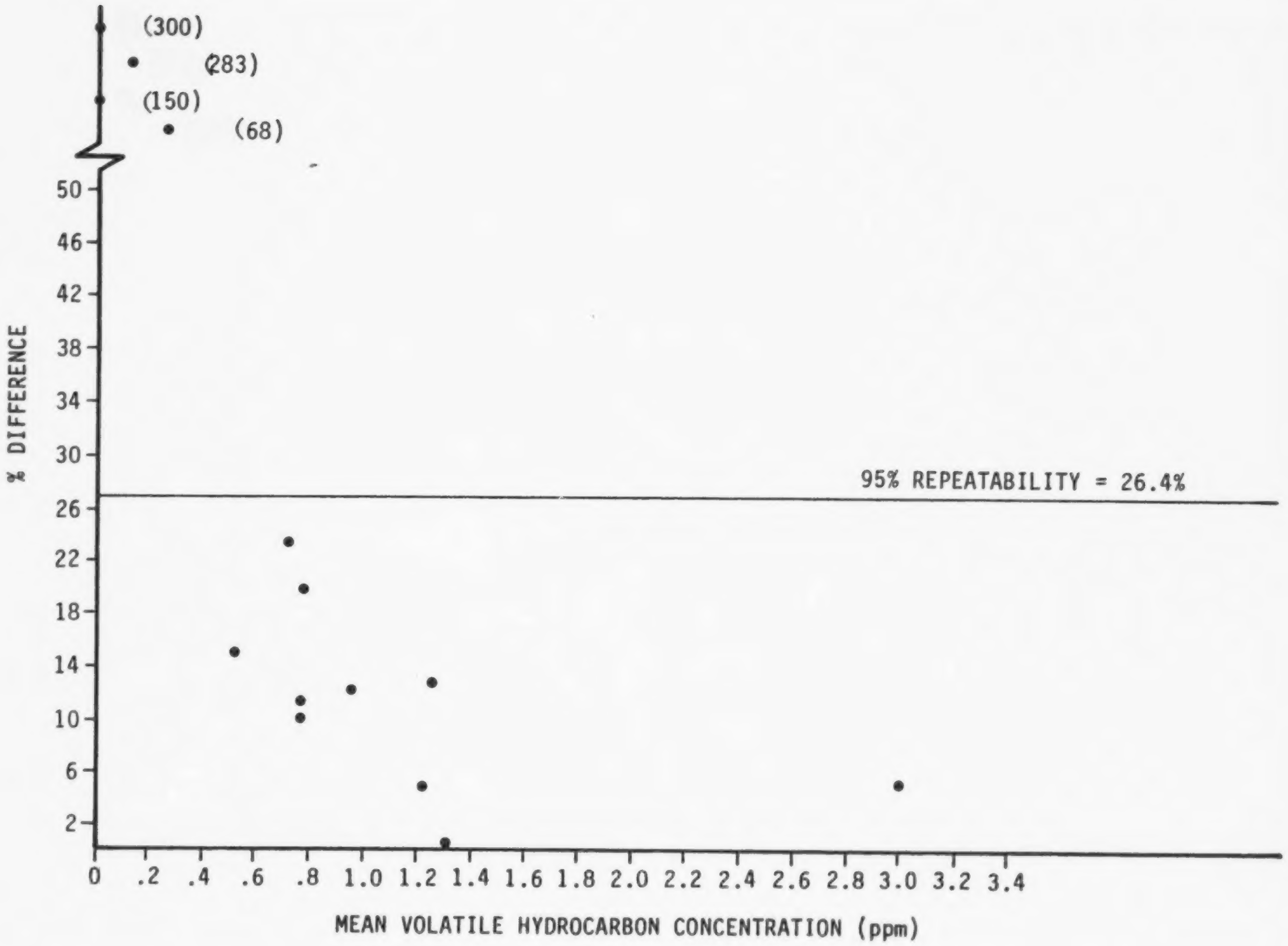


Figure C4-9. Repeatability of Gravimetric Determination

measurement devices calibrated prior to sampling. During sampling, equipment was monitored continuously for proper operation.

One of the most important methods involved to assure that a proper sample is obtained is the calibration of sample volume metering devices. In this program the devices used are dry gas meters and rotameters. The dry gas meter used in the EPA Method 5 train was calibrated generally in conformance to EPA's publication Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment.[6] Instead of using a wet test meter as a standard, a Hastings Model AHL-5 flowmeter was used. This instrument traveled much better than a wet test meter and calibration of the unit remained constant. Calibration was performed over a similar range as suggested in the above publication and calibration correction factors for the gas meter and orifice meter in the sampling unit were calculated according to suggested procedures. Similarly, the gas meter in the SASS train was calibrated but only at one flow rate, close to the expected constant sampling rate. Meter correction factors were calculated. The rotameter in the grab sampling train was checked rather than calibrated as any differences in the measured range of rates between the rotameter and the standard were negligible.

Proper operation of equipment was monitored continuously during all sampling activities. Equipment was shut down, inspected, and repaired if required, before continuing sampling. Upon completion of sampling, great care was taken with sampling containers in order to eliminate contamination of the samples prior to analysis in the laboratory trailer.

The primary quality control procedure during the analysis of the stack samples was the analysis of standards. The various methods used in the chemical analysis of these samples is described in detail in Appendix A, "Sampling Methodologies." Blind standards were analyzed for aldehydes, sulfur gases, and NO_x. Table C4-1 contains the results of these standard analyses. Figures C4-10 and C4-11 show the percent difference from the standard plotted versus the standard concentration for the aldehyde and sulfur species standards.

The percent differences for the 28 aldehyde standard analyses average 0.8 percent with a standard deviation of 5.2 percent. The variability appears greater at the lower concentration levels (about ± 12 percent) than for the higher concentration standards (about ± 6 percent). The aldehyde analysis procedure is concluded to be unbiased with a precision averaging about ± 10 percent.

The percent differences for the 18 sulfur analyses averaged 0.5 percent with a standard deviation of 14.6 percent. Only two standards above 100 ppm were tested. The percent differences ranged from - 39 to + 20 percent, but only 3 of the 18 analyses were low. The overall accuracy (including both bias and precision) of the method for concentrations below 100 ppm is about ± 30 percent.

The three standard analyses for NO_x ranged from 21 to 73 percent low, indicating potential inaccuracies in the analytical method utilizing potassium dichromate-aqueous sulfuric acid solution. A chromotropic acid method of

TABLE C4-1. BLIND STANDARDS FOR STACK SAMPLE ANALYSIS

ALDEHYDE STANDARDS

KNOWN	MEAS	DIFF	PDIFF
406.8	447.6	-40.8	-10.029
406.8	440.5	-33.7	-8.284
806.0	871.0	-65.0	-8.065
406.8	426.3	-19.5	-4.794
4068.0	4210.0	-142.0	-3.491
406.8	412.1	-5.3	-1.303
4068.0	4121.0	-53.0	-1.303
4068.0	4103.0	-35.0	-0.860
4068.0	4103.0	-35.0	-0.860
4068.0	4103.0	-35.0	-0.860
4068.0	4085.0	-17.0	-0.418
406.8	405.0	1.8	0.442
406.8	405.0	1.8	0.442
406.8	405.0	1.8	0.442
4068.0	4050.0	18.0	0.442
4068.0	4050.0	18.0	0.442
4068.0	4032.0	36.0	0.885
4068.0	4032.0	36.0	0.885
406.8	397.9	8.9	2.188
4068.0	3961.0	107.0	2.630
4068.0	3943.0	125.0	3.073
806.0	772.0	34.0	4.218
4068.0	3854.0	214.0	5.261
4068.0	3854.0	214.0	5.261
806.0	738.0	68.0	8.437
406.8	369.5	37.3	9.169
96.8	87.0	9.8	10.124
403.0	357.0	46.0	11.414

SULFUR SPECIES STANDARDS

KNOWN	MEAS	DIFF	PDIFF
9.37	13.00	-3.63	-38.741
17.90	22.40	-4.50	-25.140
48.30	56.00	-7.70	-15.942
3.25	3.30	-0.05	-1.538
6.50	6.50	0.00	0.000
202.00	201.00	1.00	0.495
12.00	11.93	0.07	0.583
12.00	11.87	0.13	1.083
9.10	9.00	0.10	1.099
12.00	11.80	0.20	1.667
30.70	30.10	0.60	1.954
352.00	338.00	14.00	3.977
40.00	37.90	2.10	5.250
7.80	7.00	0.80	10.256
5.28	4.58	0.70	13.258
4.00	3.40	0.60	15.000
12.80	10.70	2.10	16.406
6.60	5.30	1.30	19.697

NO_x STANDARD

KNOWN	MEAS	DIFF	PDIFF
203	160.0	43.0	21.1823
544	357.0	187.0	34.3750
99	26.6	72.4	73.1313

Known - Concentration of standard, ppm

Meas - Measured concentration

Diff - Known - Measured

PDIFF - Diff X 100/Known

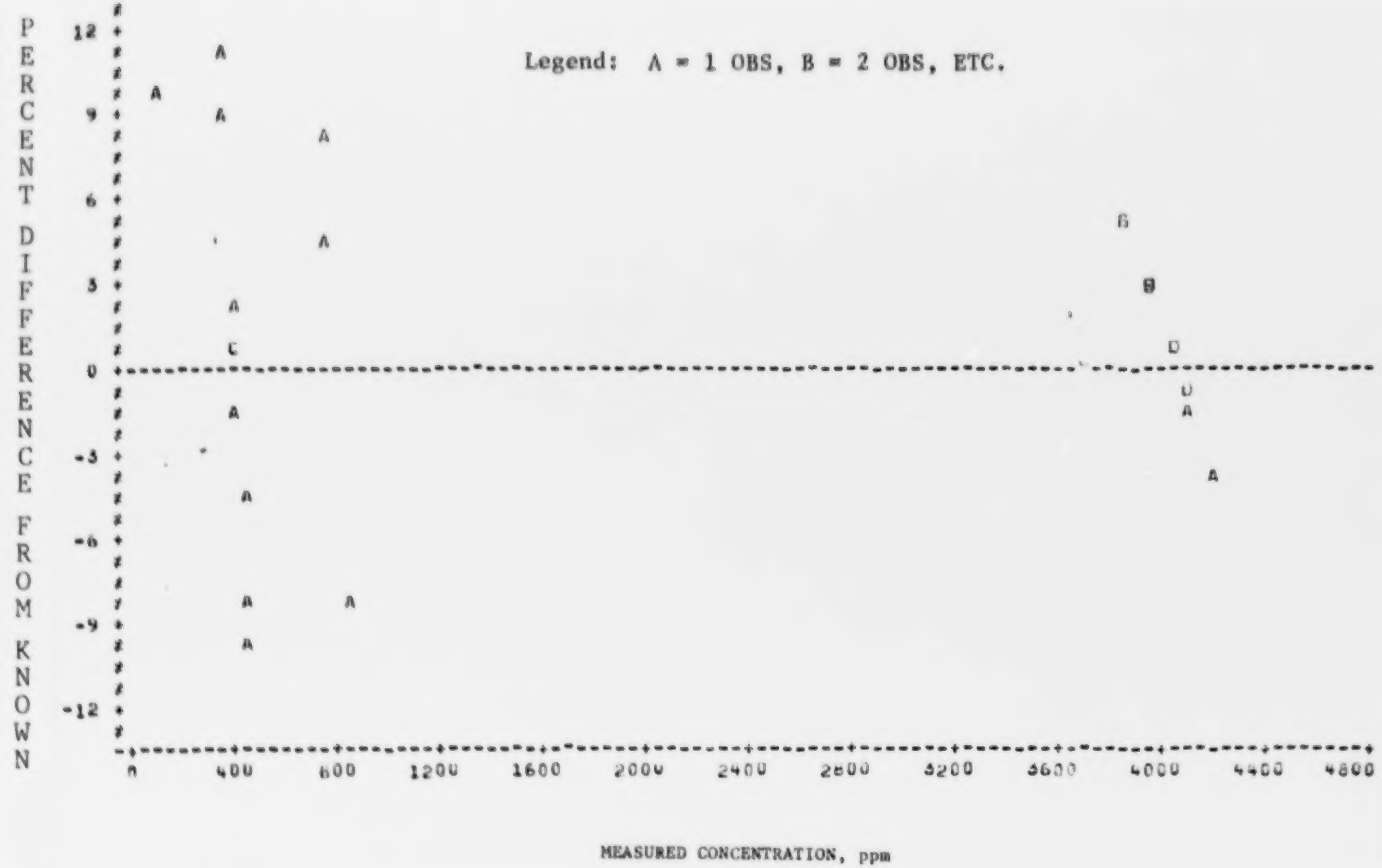


Figure C4-10. Blind Standards Analysis - Aldehydes

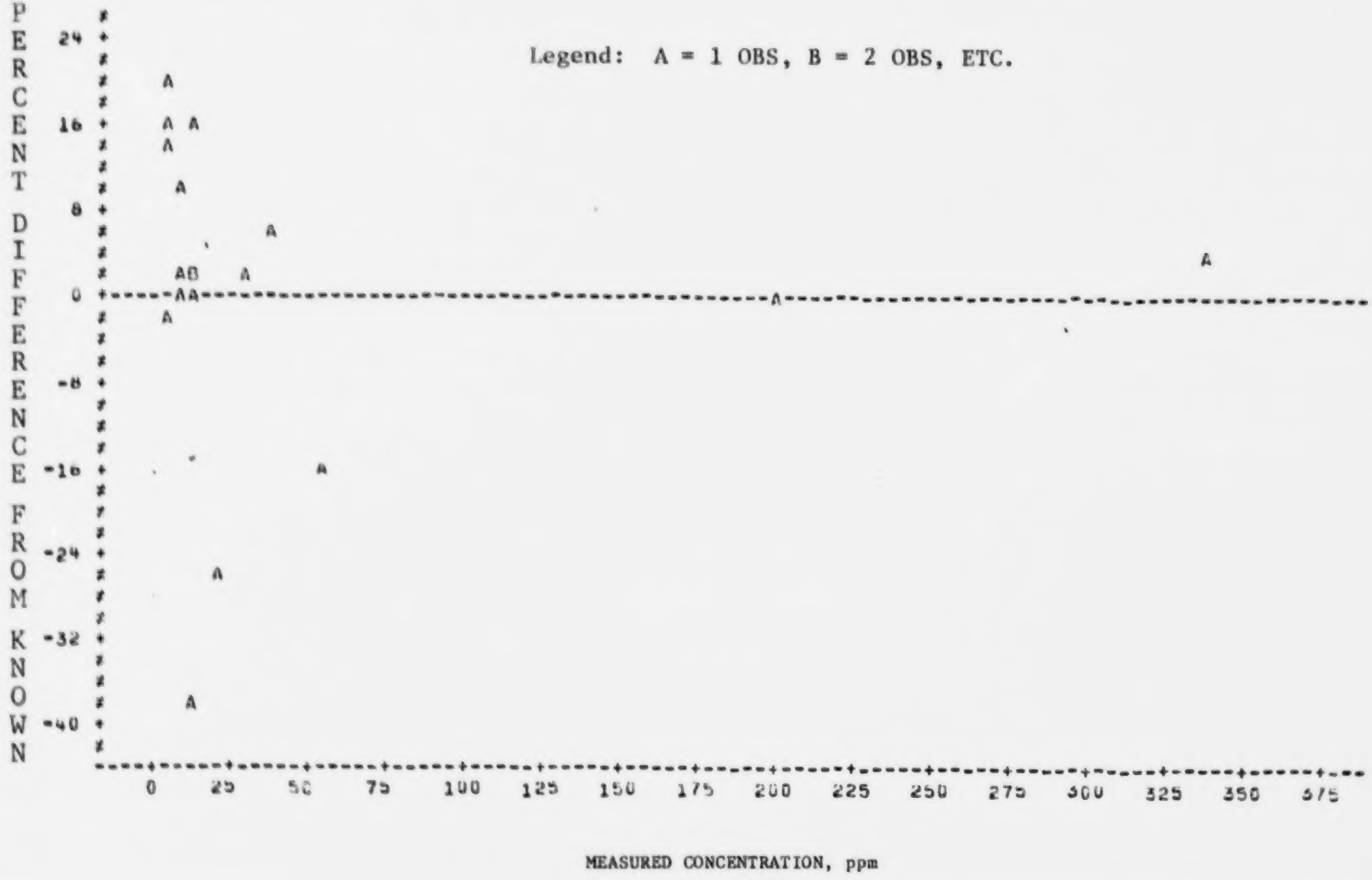


FIGURE C4-11. Blind Standards Analysis - Sulfur Gases

analysis was tried. This method was finally used exclusively because it appeared to be more reliable and accurate than the potassium dichromate method.

5.0 DATA QUALITY CONTROL AND VALIDATION

A comprehensive data base management system was required to handle the data generated in this program. The total data obtained during the program resulted in more than one-half million records. Initially data was loaded into sequential files on a UNIVAC 1108 system. As requirements for statistical analysis, reporting, editing, and other data manipulations increased, it became necessary to obtain a data management/analysis software package.

The SAS system on Boeing Computer Corporation's IBM 370-168 TSO system was used to manage and analyze the data after six refineries were completed. SAS offered extensive statistical procedures, as well as data manipulation capabilities. The data base was kept on on-line disk storage with weekly backups on tapes.

5.1 Data Collection and Coding

Formatted data sheets were provided for field and laboratory use in recording all data. These forms were designed so that keypunching could be done directly from the original sheets, thus eliminating transcription errors. Data sheets were collected daily in the field and reviewed by the field supervisor for completion and general accuracy. At the end of sampling at each refinery, the completed forms were hand-carried to Radian, sorted, and immediately bound in notebooks. Then a data analyst reviewed each form and completed the coding of certain variables. Next the data sheets were keypunched and verified.

5.2 Computer Files

Sequential files of data were developed for each of the source types studied. The data were validated during the loading process by the following means:

- Each variable was checked for appropriate numeric or alphanumeric characters.
- An acceptable "range of values" was checked for each variable. These were established by knowledge of possible codes as well as engineering judgment on process variables.
- All leak rates were calculated by computer code in the load program. The computed leak rates were printed out and compared to previously hand calculated values.
- Each variable in a data record was assigned weights describing the importance of the variable toward using the data record (e.g., unit and ID were considered essential variables). The weights were used to produce an error report after each data file was loaded. The records with a large error code were checked and corrections made by referring to the original data sheets.

5.3 Quality Control Checks

After a new data file was created, a number of reports were prepared for both reporting and quality control purposes. The entire data set was printed in an easily readable format for future reference. Selected key variables were printed out in a report. This report was checked against the original field data, in some cases laboratory notebooks, by a data analyst. A formatted report of process variables and leak rate data was prepared, reviewed by Radian engineers, and sent to the refinery from which the data were collected for further revision and verification.

A number of statistical reports were run to further validate the data. A report generated the mean, standard deviation, minimum, and maximum for each variable in each refinery. Another report generated sample correlation statistics for all combinations of continuous variables. Two-way plots and frequency tables were produced for each process variable and the leak rate. Control charts were used to display laboratory measurements made over time. All of these plots and reports were studied for potential outliers and for possible trends and relationships among the variables.

5.4 Data Analysis Files

After the data from each refinery had been validated, an "analysis" data base was developed. This data base was used to produce summary reports, develop correlations, develop emission factors, and to do statistical analyses to summarize the progress of the project. A number of new variables such as the process stream classifications were created as the analysis data base was produced.

Other operations performed on the data sets included:

- Leak rates from any quality control samples on each source were averaged with the original sample result to get one average leak rate for each individual source.
- A process stream classification variable was created from individual process stream codes.
- Logarithms of both leak rate and screening values were produced.
- Data sets with critical missing parameters were omitted from the files.
- Summary statistics of screening values such as the average and maximum value were developed and included in the data base.
- The files were sorted by units and leak rates within units. This consolidated the data from each refinery into summary files.

Additional specific data bases were created to handle particular aspects of the program. These include:

- a short-term maintenance file for valves selected in the last four refineries (and at Refinery "F") for maintenance study,
- a file of leak rate quality control data, and
- special study data files.

These files are currently kept on disk storage for quick analysis, reporting, and editing. Each file is backed up on a weekly basis on tape. Editing is done either by updating the central file and recreating the data bases, or by updating the individual data bases as well as the central file.

6.0 STATISTICAL PROCEDURES FOR ANALYZING EMISSIONS DATA

A number of statistical analysis procedures were used in analyzing the emissions data developed during this program. The discussions in the previous sections have shown that hydrocarbon measurements were not very precise (precision was usually greater than ± 50 percent) and that variability of leak rates from different sources spanned several orders of magnitude. This extreme variability made the use of properly selected statistical models and techniques very important in extrapolating the data collected during this program to the population of fugitive emissions.

The estimation of emission factors was one important objective of this program. Because of the high degree of skewness in the distribution of nonmethane leaks rates from baggable sources, conventional statistics were inadequate for efficient estimation of emission factors and their variances. In addition to the skewness, a large percentage of the sources studied were considered "nonleaking" (i.e., had a screening value < 200 ppm). These sources affect the emission factor and therefore had to be considered in developing estimates for these factors. Another statistical problem which had to be addressed in developing the emission factors was the estimation of leak rates for sources which screened greater than or equal to 200 ppmv but were not sampled for economic reasons.

The population to which the data from this study can be extrapolated is the total number of sources from all United States refineries. The selection procedure for sources was described in Appendix A of this report. For this analysis, it is assumed that a random selection was made for refineries, units within a refinery, and sources within a specific choice variable category within a unit. The "true value," e.g., of an emission factor, is an abstract concept. Essentially, this "true value" is that number which would be obtained if at a given point in time all sources of a particular type in the population could be sampled, analyzed and averaged.

This section discusses the statistical procedures used in the following areas:

- estimating emissions from nonsampled sources,
- statistical models for leak rate distributions,
- development of confidence intervals, and
- development of nomographs.

6.1 Estimating Emissions for Nonsampled Sources

Due to time and equipment constraints, it was not always possible to sample all sources that screened greater than 200 ppmv. At the fifth refinery, a sampling strategy was developed to reduce the sampling workload. All sources screening greater than 10,000 ppmv were sampled, but only one-fourth of the valves and pumps with screening values between 200 and 10,000 ppmv were sampled. In order not to bias the distribution of leaking sources, it was necessary to develop estimated values for all sources screening greater than 200 ppmv and not sampled. The number of sources sampled and estimated for each source type is shown in the following table:

Baggable Source Type	Total Sources Sampled or Screened > 200 ppmv	Sources Sampled	Sources to be Estimated
Valves	627	474	153
Pump Seals	382	281	101
Compressor Seals			
Hydrocarbon Service	102	83	19
Hydrogen Service	69	60	9
Flanges	62	43	19
Drains	49	28	21
Relief Valves	58	31	27

Least-squares regression analyses were done for each device type, regressing the logarithm of the nonmethane leak rate on the logarithm of the maximum screening reading. Both the original screening value and rescreening values (taken closer to the time of sampling for leak rate) were evaluated and a "best" equation was selected for each device as summarized in Table C6-1.

Using the equations in Table C6-1, predicted log-nonmethane leak rates were computed for each source not sampled with a screening value greater than or equal to 200 ppmv. Leak rates (lb/hr) were then computed using

$$\text{leak rate} = \exp_{10}\,[\log \text{leak} + z\,(\text{standard error of estimate})],$$

the number of sources estimated, where z is a random number from a standard-normal distribution. The use of the random number is an attempt to yield a predicted distribution of leak rates which would approximate the distribution if all sources

TABLE [illegible]. PREDICTION EQUATIONS FOR NONMETHANE LEAK RATES BASED ON MAXIMUM TLV SCREENING OR RESCREENING VALUES

SOURCE TYPE	LEAST - SQUARES EQUATION	NUMBER OF DATA PAIRS	CORRELATION COEFFICIENT (r)	STANDARD ERROR OF ESTIMATE
Valves	LOG(NMLR)= -3.41 + 0.88 LOG(MXTLV-RS)	177	0.78	0.736
Pump Seals	LOG(NMLR)= -4.64 + 0.89 LOG(MXTLV-RS)	171	0.68	0.820
Compressor Seals:				
Hydrocarbon Service	LOG(NMLR)= -4.77 + 0.92 LOG(MXTLV-RS)	48	0.58	0.791
Hydrogen Service	LOG(NMLR)= -1.66 + 0.44 LOG(MXTLV- S)	44	0.36	0.884
Flanges	LOG(NMLR)= -5.11 + 0.84 LOG(MXTLV- S)	47	0.74	0.535
Drains	LOG(NMLR)= -5.02 + 1.16 LOG(MXTLV- S)	60	0.72	0.807
Relief Valves	LOG(NMLR)= -4.47 + 0.87 LOG(MXTLV-RS)	53	0.78	0.637

NMLR - Nonmethane leak rate (lb/hr)
MXTLV- S - Maximum value - original screening (ppmv)
MXTLV-RS - Maximum value - rescreening (ppmv)
LOG - Logarithm, base 10

were sampled. No bias correction factor is needed in converting from the log to linear scale since the mean leak rate is not being predicted. The predicted leak rates were used in further analyses and development of emission factors.

Because the true leak rate/screening relationship is unknown, there is a potential bias introduced when these predicted leak rates are used in developing emission factors. The potential bias is proportional to the standard error of the estimates adjusted for number of data pairs used to develop the equation. The impact of the bias on emission factors depends on the percent of sources leaking. The potential bias for each source type estimated was approximated by weighting the 95 percent confidence limits of the predicted values according to the percent of estimated sources. These values were expressed as a percent of the emission factor estimate. The potential biases were found to be as follows:

POTENTIAL PERCENT BIAS IN EMISSION FACTORS FROM ESTIMATING SOURCES

Source Type	- Percent Bias	+ Percent Bias
Valves	0.9	2.4
Pump Seals	2.7	2.9
Compressor Seals		
Hydrocarbon Service	11.8	14.1
Hydrogen Service	1.6	3.2
Flanges	0.3	0.3
Drains	3.5	4.2
Relief Valves	5.1	6.0

These potential biases were taken into consideration in developing confidence intervals as discussed in Section 6.3.

6.2 Statistical Distribution Models for Leak Rates

A lognormal distribution was used to model the distribution of leaking sources. This distribution has the property that when the original data are transformed by taking natural logarithms, the transformed data will follow a normal distribution. The lognormal distribution is often appropriate when the standard error of an individual value is proportional to the magnitude of the value. The form of the lognormal distribution is as follows:

$$f(x) = \begin{cases} \dfrac{\exp\left[-\dfrac{(\ell n\ x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} & \text{for } 0 > x > \infty \\ 0 & \text{for } x \leq 0 \end{cases}$$

$$\text{Mean} = \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = \exp[2\mu + 2\sigma^2] - \exp[2\mu + \sigma^2]$$

In order to develop estimates for emission factors, the nonleaking sources (leak rate assumed equal to zero) also had to be modeled. A mixed distribution, specifically a lognormal distribution with a discrete probability mass at zero, was used for this purpose. Letting ρ equal the fraction of nonleaking sources in the population, this mixed-lognormal distribution has the following form:

$$f(x) = \begin{cases} \dfrac{(1-\rho)\ \exp\left[-\dfrac{(\ell n\ x - \mu)^2}{2\sigma^2}\right]}{x\sigma\sqrt{2\pi}} & \text{for} \quad 0 < x < \infty \\ \rho & \text{for} \quad x = 0 \\ 0 & \text{for} \quad x < 0 \end{cases}$$

$$\text{Mean} = (1 - \rho)\ \exp\left[\mu + \frac{\sigma^2}{2}\right]$$

$$\text{Variance} = (1 - \rho)\ [\exp(2\mu + \sigma^2)]\ [\exp(\sigma^2) - (1 - \rho)]$$

Efficient estimates of the mean and variance of the population model by this mixed distribution have been developed [Finney[3] (1941), Aitchison[1] (1955)]. These estimates are as follows:

The best, unbiased estimator of the population mean emission rate is

$$m = \left\{ \left(1 - \frac{r}{n}\right) \exp\ (\bar{x}) \quad g\left(\frac{s^2}{2}\right) \right\}$$

and the best, unbiased estimator of the population variance of the emission rates is

$$v = \left(1 - \frac{r}{n}\right) \exp(2\bar{x}) \left[g(2s^2) - \left(1 - \frac{r}{n-1}\right) g\left(\frac{n-r-2}{n-r-1}\ s^2\right)\right]$$

where

n = number of sources screened

r = number of sources screened < 200 ppm or with measured leak < 10^{-5} lbs/hr

m = $n - r$ = number of "leaking" sources

$g(t)$ = infinite series

$$= 1 + \frac{(m-1)t}{m} + \frac{(m-1)^3 t^2}{m^2 2!\ (m+1)} + \frac{(m-1)^5 t^3}{m^3 3!(m+1)\ (m+3)} \cdots .$$

$\bar{x}$ = average of the logarithm of leak sources

$$= \sum_{1}^{n-r} \ell n \text{ (nonmethane leaks)}/(n-r)$$

s^2 = variance of the logarithm of leaking sources

$$= \sum_{1}^{n-r} [\ell n \text{ (nonmethane leaks)} - \bar{x}]^2/(n-r-1).$$

The mean and variance formulas hold whenever there is more than one leaking source $(n - r > 1)$. When only one leaking source is identified, the following estimates are appropriate:

$$\text{mean} = \frac{x_1}{n} \text{ and variance} = \frac{x_1^2}{n} ,$$

where x is the single measured leak. If no leaks are found $(r = n)$, then the best estimate for both the mean and variance is zero.

Computer programs were developed for these estimators and the estimator for the mean was used for all emission factors presented in this publication. Finney[3] (1941) showed that this estimator is more than twice as efficient as the arithmetic mean for data distributed similarly to the leak rates from baggable sources.

Since data distributed lognormally can be transformed to a normal distribution by taking natural logarithms of the data, the distribution assumption for the leaking sources can be tested by examining distributions of the log leak rates. Histograms displaying these distributions were constructed for all important source type and process stream classifications and are shown in Figures C6-1 through C6-12. The data for most sources appear to adequately approximate a normal distribution. The compressor seal data from hydrocarbon service and the heavy stream data for pump seals both appeared skewed to the left. Compressor seals with sampled leak rates less than 10^{-3} lb/hr were considered as negligible (zero) to minimize this skewness.

To statistically test the assumption of a normal distribution for the log-leak rates, skewness and kurtosis statistics were computed for each data group and tested for departures from their expected value of zero in a normal distribution. Table C6-2 summarizes these statistics.

Only three of the twelve cases indicate significant lack of normality, confirming the conclusions from the histograms.

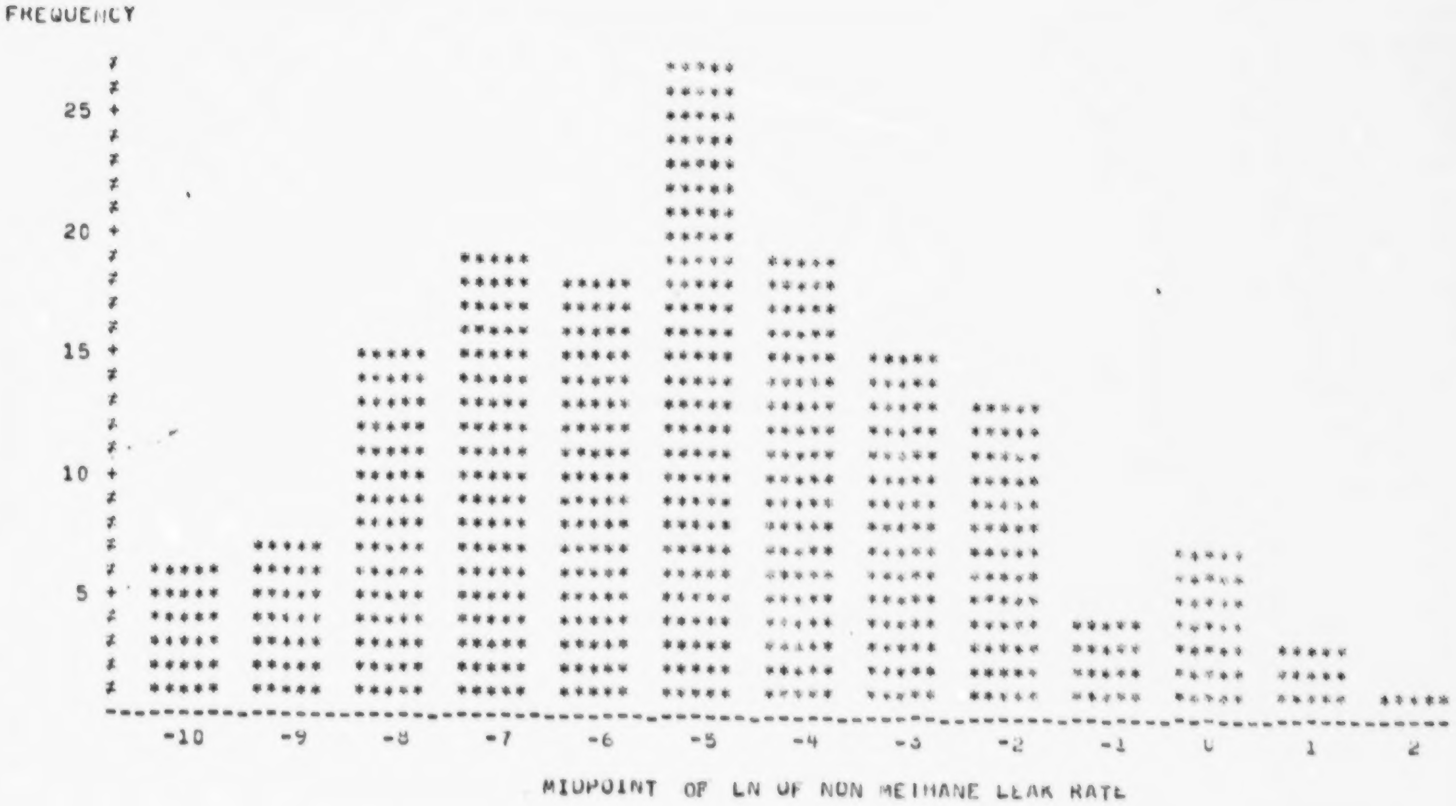


Figure C6-1. Histogram of Ln of Nonmethane Leak Rate Valves
Gas/Vapor Streams

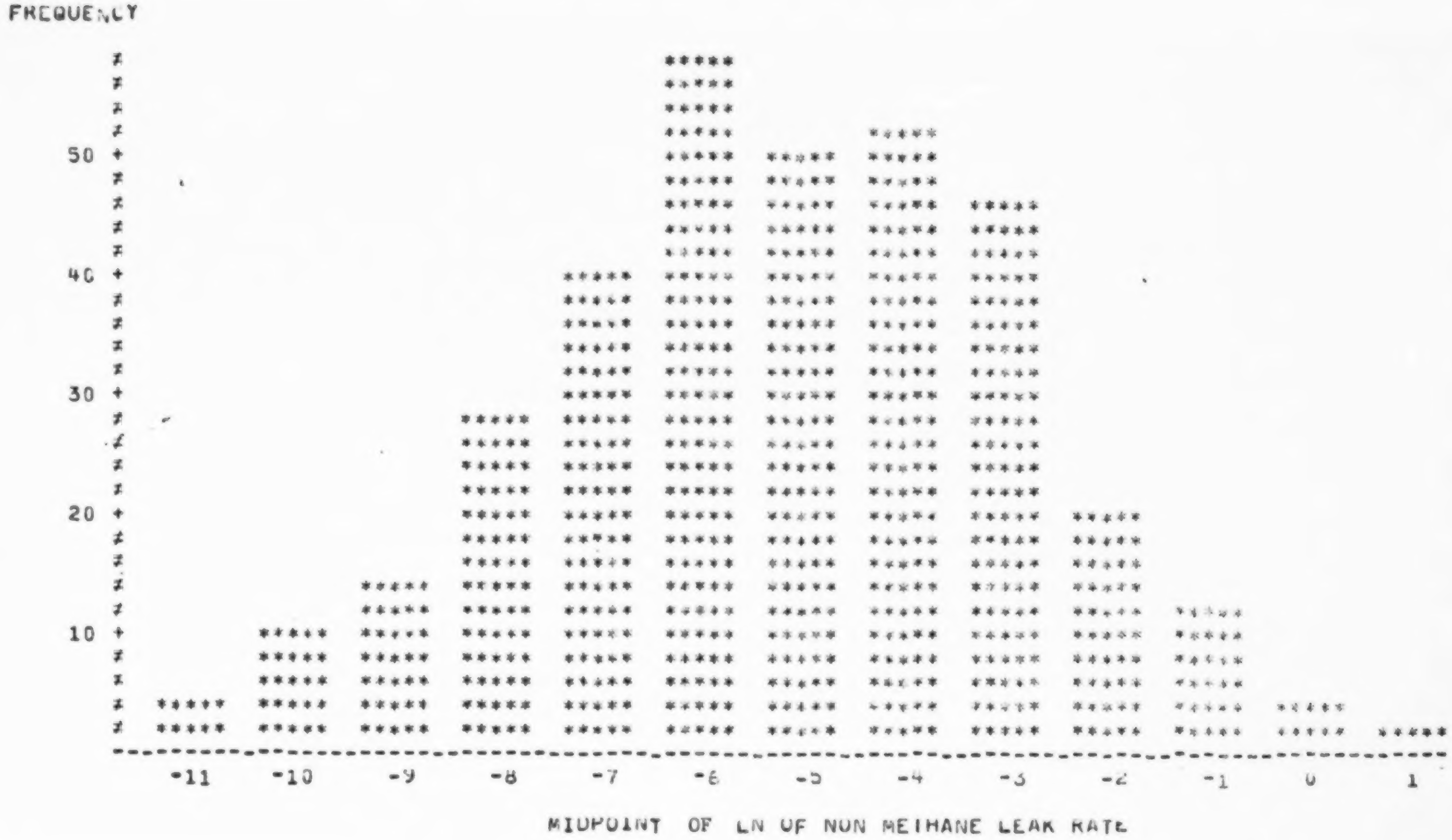


Figure C6-2. Histogram of Ln of Nonmethane Leak Rate Valves
Light Liquids/Two-Phase Streams

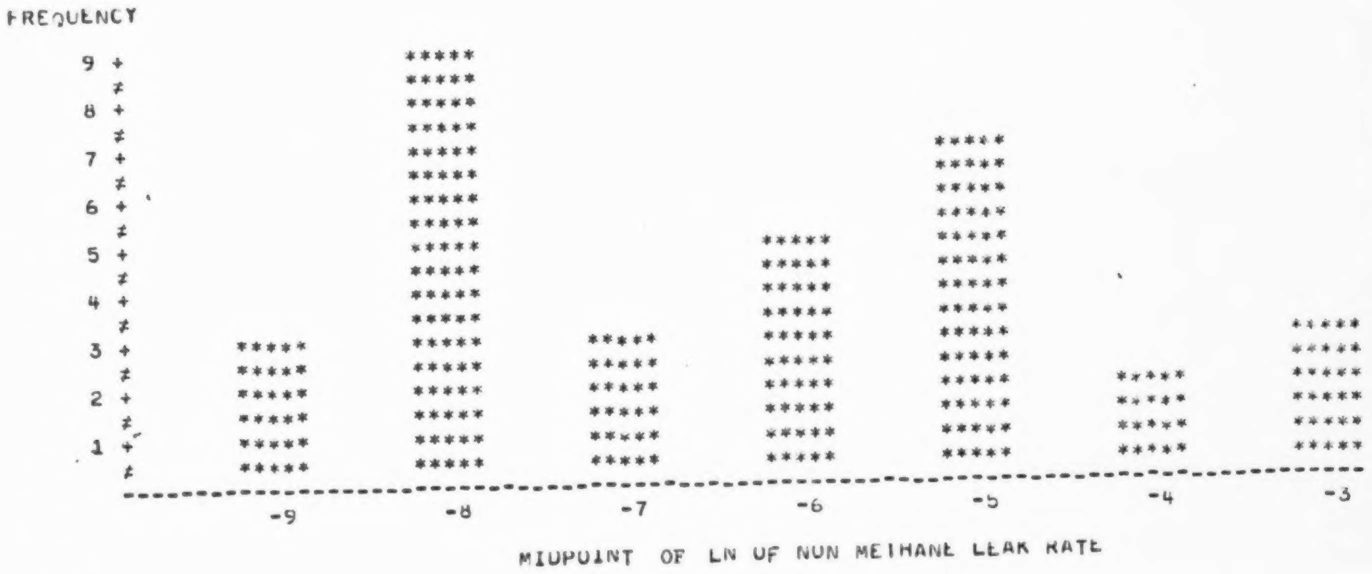


Figure C6-3. Histogram of Ln of Nonmethane Leak Rate Valves
Heavy Liquid Streams

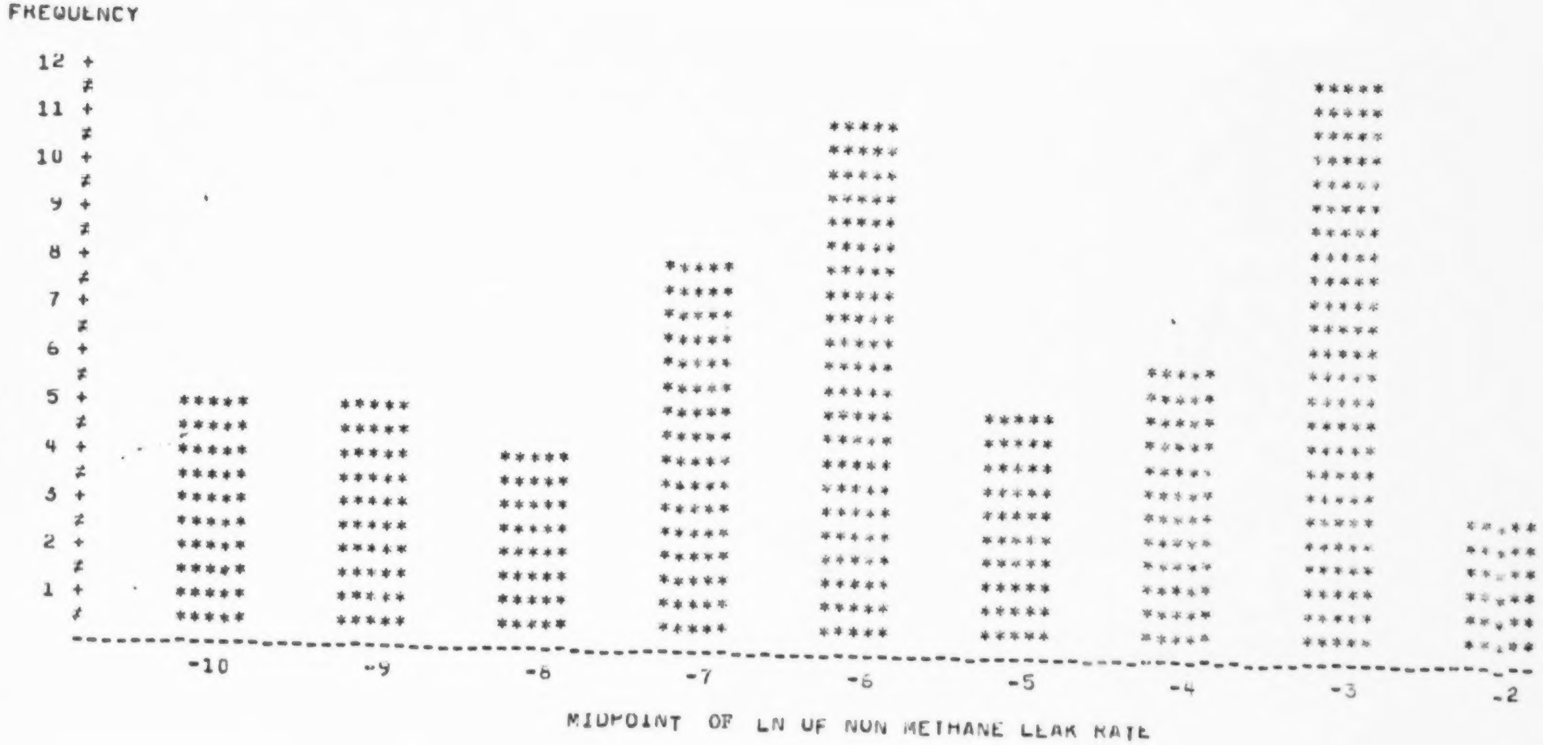


Figure C6-4. Histogram of Ln of Nonmethane Leak Rate Valves
Hydrogen Streams

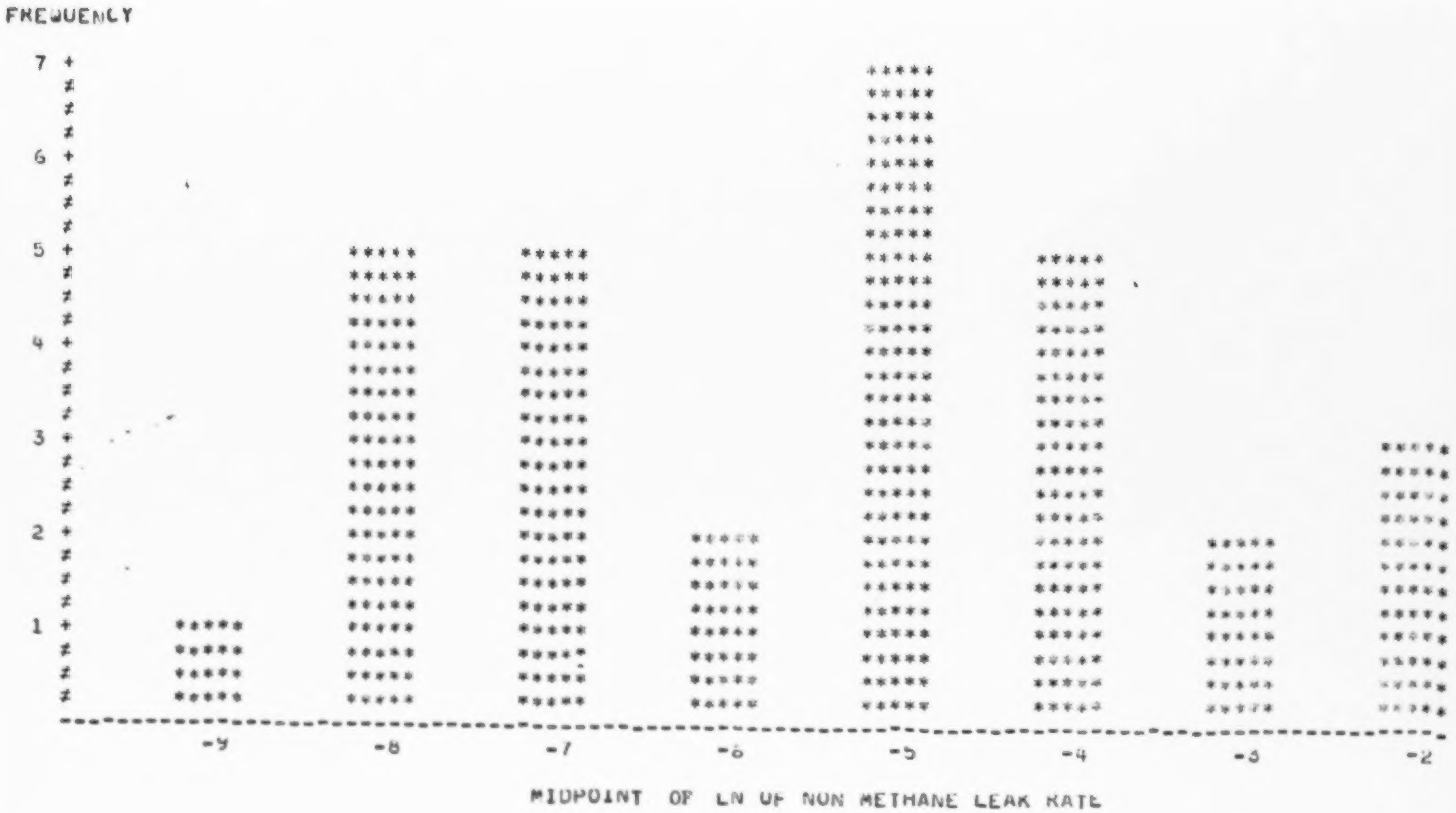


Figure C6-5. Histogram of LN of Nonmethane Leak Rate
Open-Ended Valves

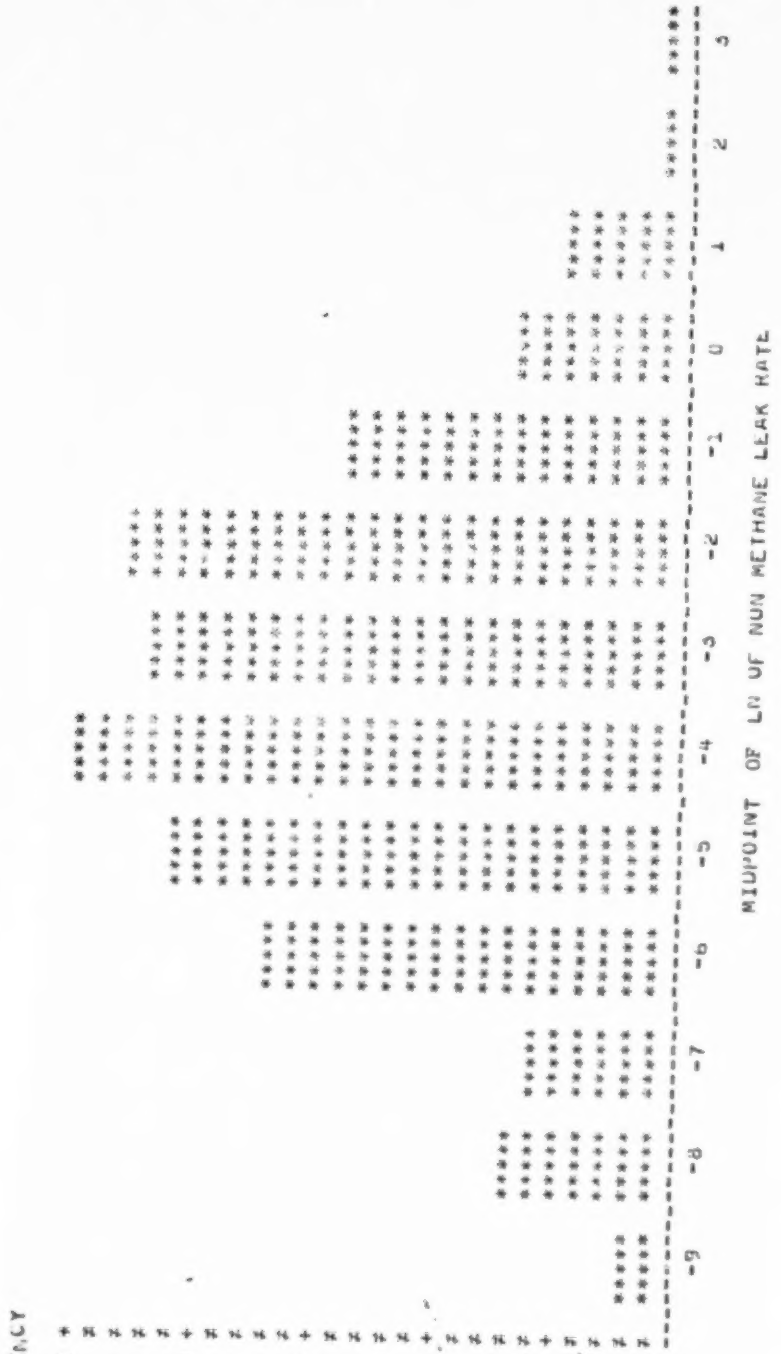


Figure C6-6. Histogram of Ln of Nonmethane Leak Rate Pump Seals Light Liquid Streams

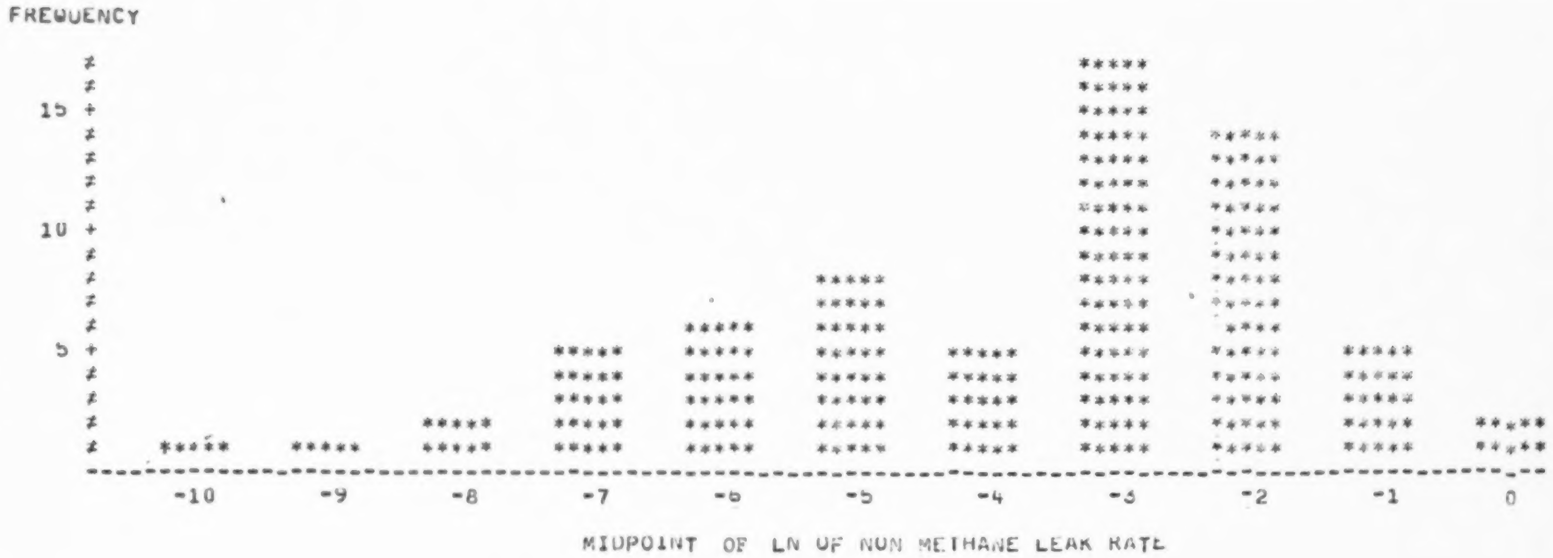


Figure C6-7. Histogram of Ln of Nonmethane Leak Rate Pump Seals
Heavy Liquid Streams

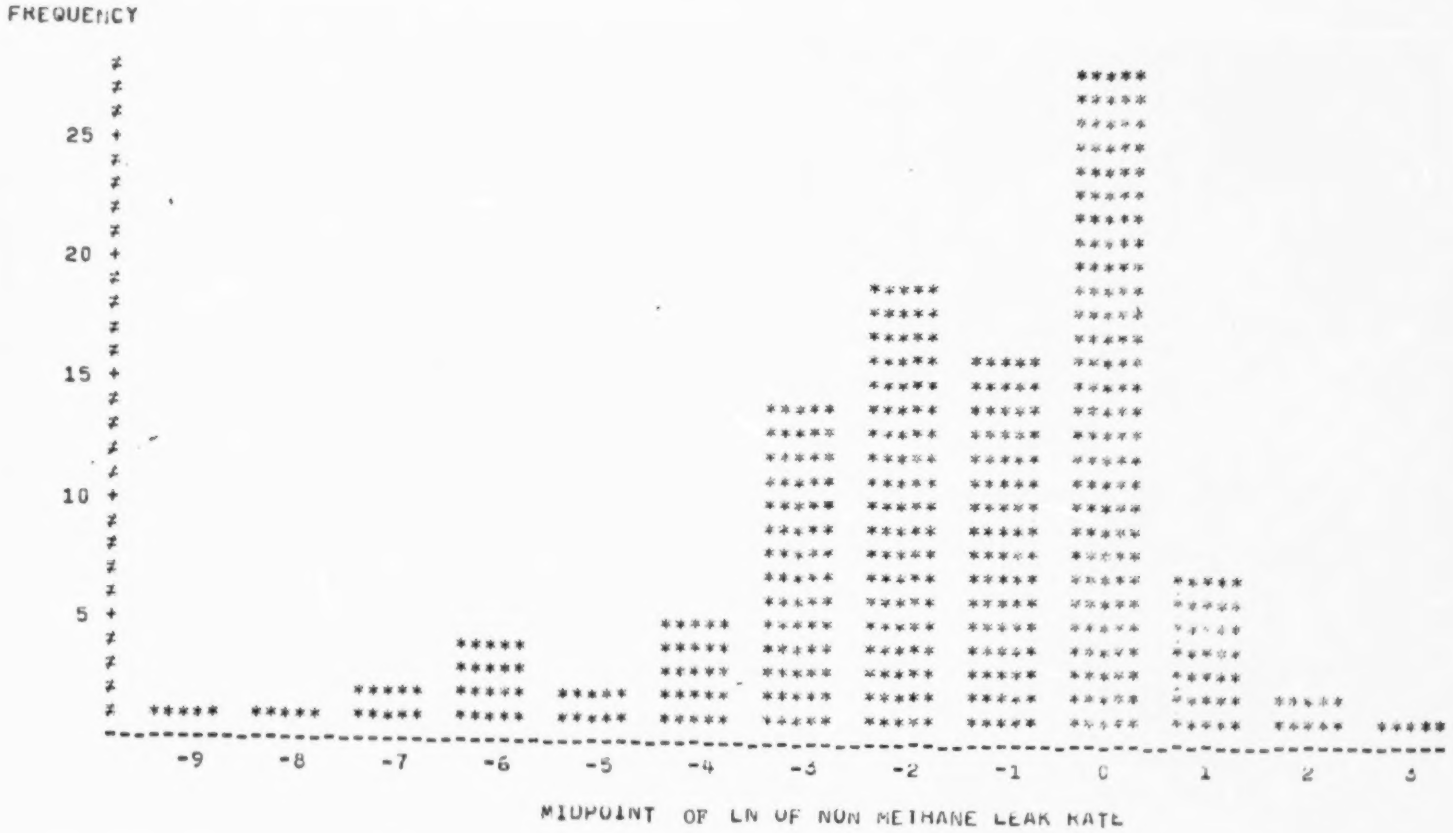


Figure C6-8. Histogram of Ln of Nonmethane Leak Rate Compressor Seals Hydrocarbon Service

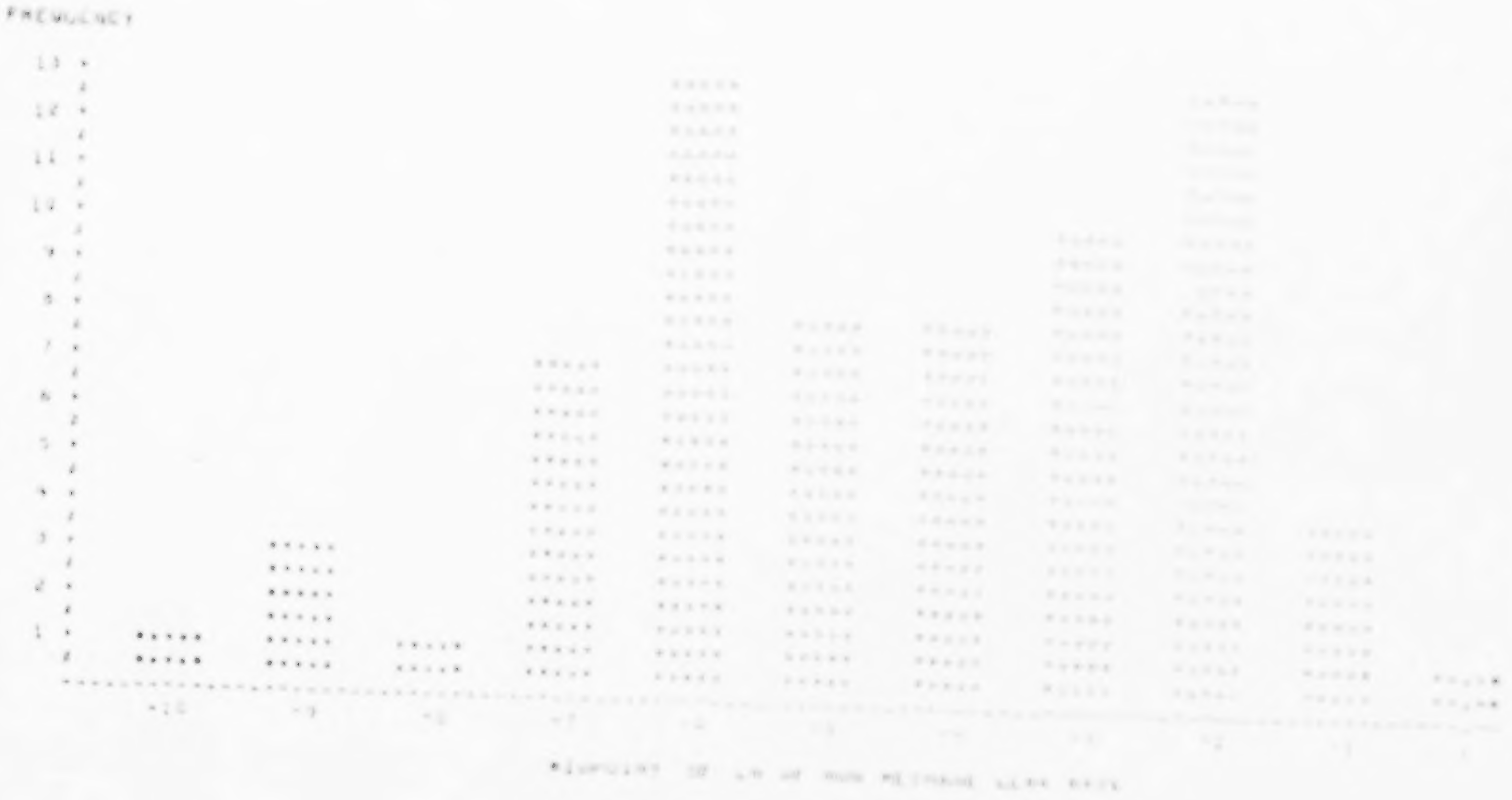


Figure C6-9. Histogram of LN of Normalized Leak Rate Compressor Seals
Hydrogen Service

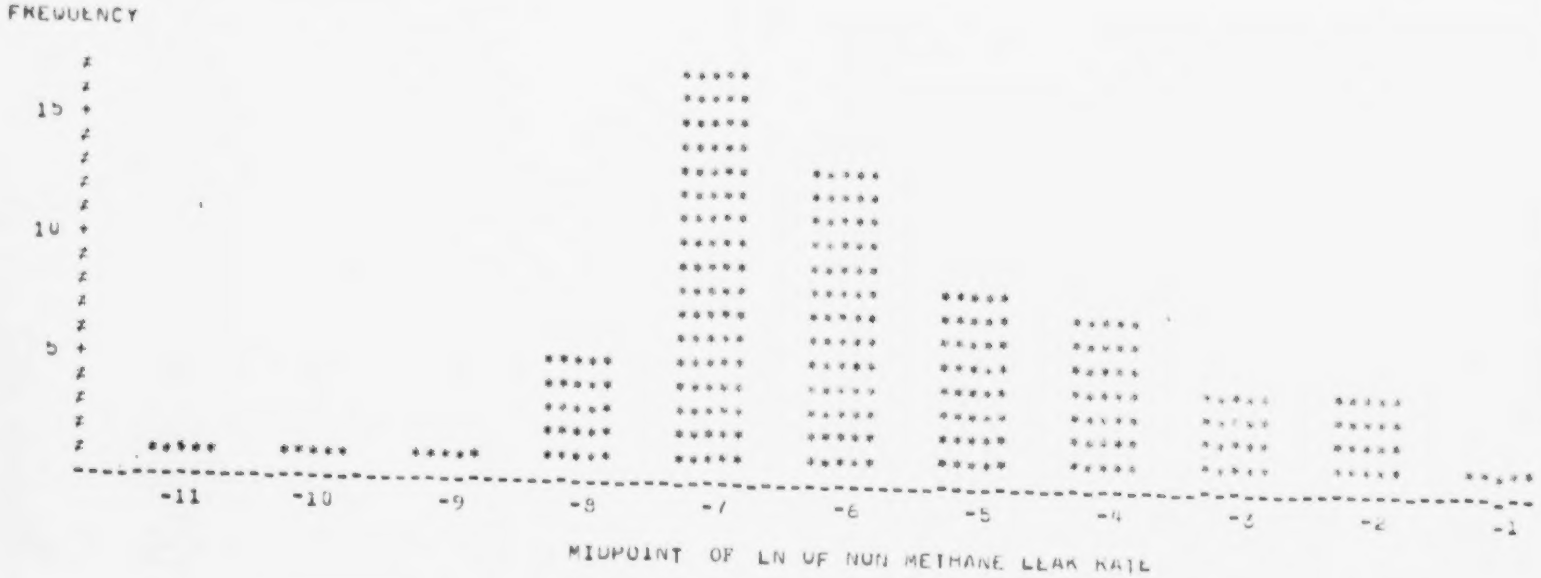


Figure C6-10. Histogram of Ln of Nonmethane Leak Rate Flanges - All Streams

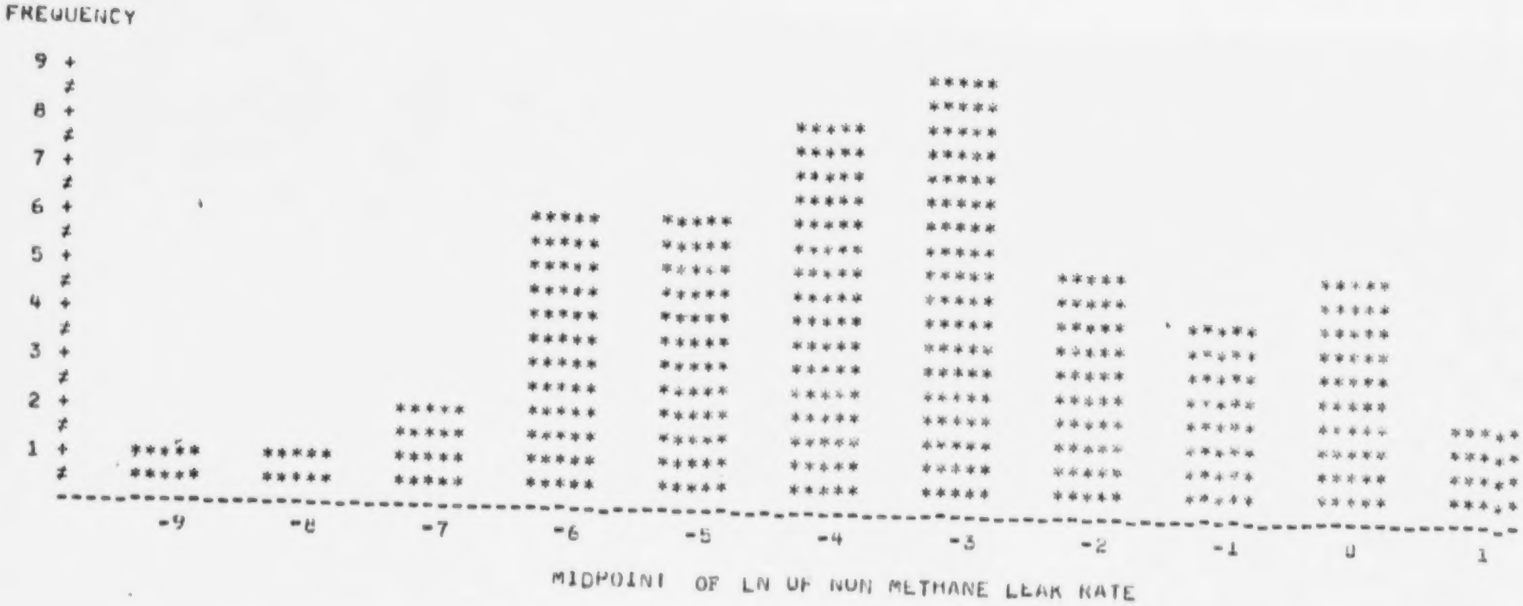


Figure C6-11. Histogram of Ln of Nonmethane Leak Rate Drains - All Streams

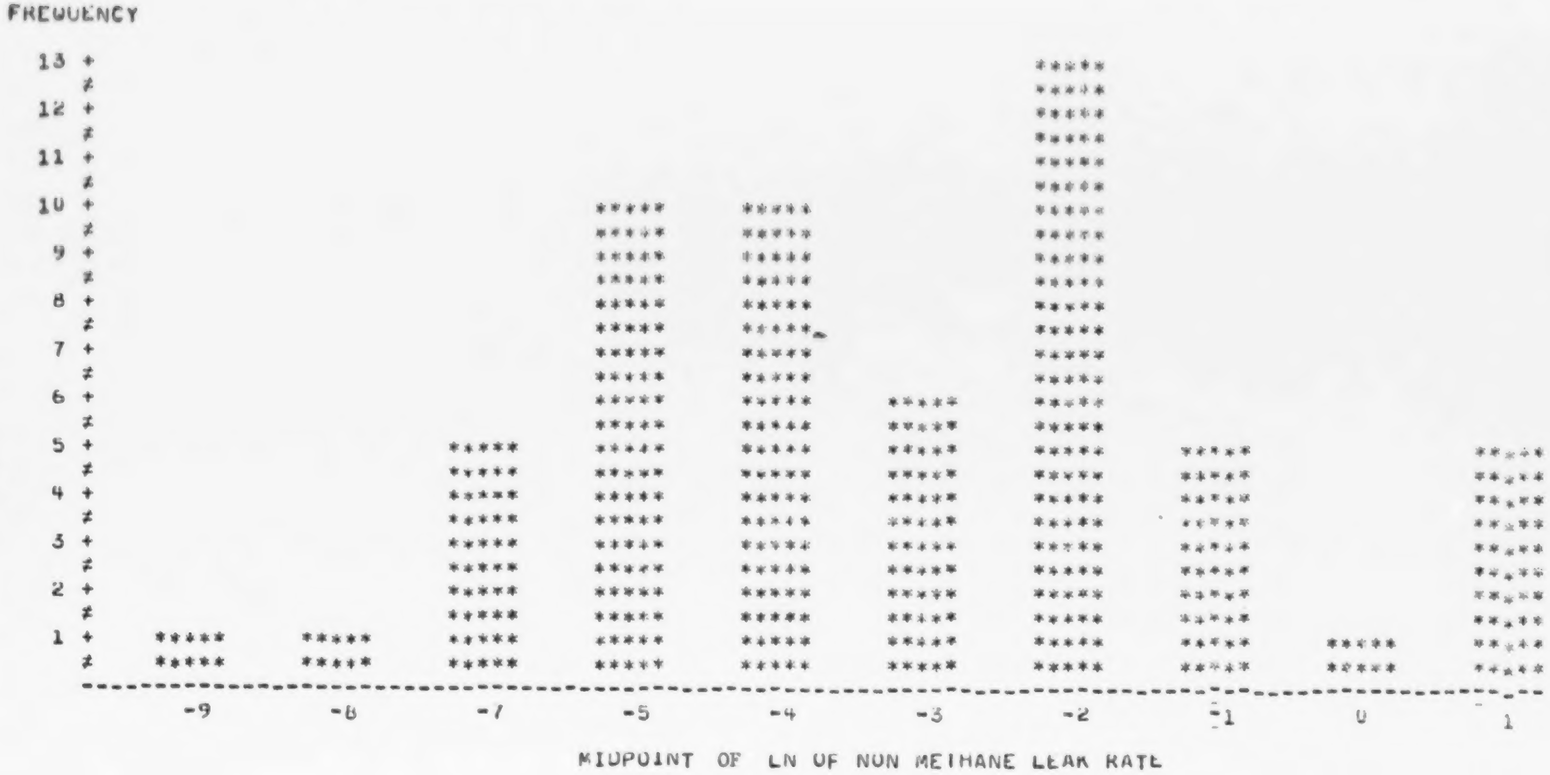


Figure C6-12. Histogram of Ln of Nonmethane Leak Rate Relief Valves - All Streams

TABLE C6-2. SKEWNESS AND KURTOSIS STATISTICS

Source Type/Stream Group	Number of Leaking Sources	Skewness	Kurtosis
Valves[1]			
Gas/Vapor Streams	154	0.19	- 0.33
Light Liquids/Two-Phase	330	- 0.16	- 0.18
Heavy Liquids	32	0.28	- 0.88
Hydrogen Streams	59	- 0.18	- 1.09*
Open-ended Valves	30	- 0.01	- 0.98
Pump Seals[1]			
Light Liquids	296	0.03	- 0.36
Heavy Liquids	66	- 0.77*	0.06
Compressor Seals			
Hydrocarbon Service	102	- 0.99*	1.16*
Hydrogen Service	69	- 0.29	0.69
Flanges	62	0.39	0.20
Drains	49	- 0.04	- 0.47
Relief Valves	58	- 0.05	- 0.21

*Probability < 0.05 given a normal distribution.

[1] All data needed to classify sources into stream type were not available for all pump seals and valves. Those particular sources are not included in this analysis.

TABLE C6-3. LEAK RATES FOR SOURCES SCREENING LESS THAN 200 PPM.

Source Type	# Sampled <200ppmv	MAX TLV (ppmv)		Leak Rates (lb/hr)			% of Total Sources Screened <200
		Minimum	Maximum	Minimum	Median	Maximum	
Compressor Seals	3	0	140	0.00086	0.00416	0.1058	23.5
Drains	5	0	120	0.00056	0.00197	0.1078	81.8
Flanges	5	0	110	0.00007	0.00056	0.0047	96.9
Pump Seals	12	8	180	0.00006	0.00137	0.0052	51.5
Relief Valves	8	40	180	0.00037	0.00132	0.0765	60.8
Valves	30	0	190	0.00001	0.00042	0.0383	67.2

TABLE C6-4. IMPACT OF "ZERO LEAK RATE" ASSUMPTION ON EMISSION FACTOR

Source	Approximate Emission Factor Estimate (lb/hr)	Median leak rate for <200 sources lb/hr	Median Times % of Sources <200 Expressed as Percent of Emission Factor
Compressor Seals	0.8	0.00098	0.1
Drains	0.07	0.00161	2.3
Flanges	0.00058	0.00054	92.8
Pump Seals	0.17	0.00071	0.4
Relief Valves	0.19	0.00080	0.4
Valves	0.023	0.00029	1.2

and each item is classified into one of two categories (leaking or nonleaking here). Exact confidence limits (level $1-\alpha$) for the estimate of percent leaking can be obtained by iteration solving for P_ℓ in

$$\sum_{i=k}^{n} \binom{n}{i} P_\ell^i \, (1-P_\ell)^{n-1} = \frac{\alpha}{2}$$

for the lower limit and for P_u in

$$\sum_{i=0}^{k} \binom{n}{i} P_u^i \, (1-P_u)^{n-i} = \frac{\alpha}{2}$$

for the upper limit, where

n = number of sources screened

k = number of leaking sources.

Tables of these solutions, available for most cases, were used to develop 95 percent confidence intervals for reporting and for computing 97.5 percent confidence intervals which were used in developing confidence intervals for emission factors. The 97.5 percent was selected so that 95 percent confidence intervals for emission factors would result when the estimated percent leaking was combined with the estimated mean leak rate ($0.975 \times 0.975 \simeq 0.95$).

Patterson[4] (1966) described how confidence intervals for the mean from a lognormal distribution can be computed using estimators developed by Finney[3] (1941). The 97.5 percent confidence intervals were computed for the average, $\bar{y}$, of the transformed data, $y = \ell n$ (leak), using

$$C_\ell = \text{lower limit} = \bar{y} - 2.24\ [s^2/(n-r)]^{1/2}$$

and

$$C_u = \text{upper limit} = \bar{y} + 2.24\ [s^2/(n-r)]^{1/2}$$

where

s^2 = the variance of the transformed data

$n - r$ = the number of leaking sources.

Then, following Patterson's arguments, confidence intervals for the mean leak rate can be computed using:

$$C'_\ell = \text{lower limit} = \exp[C_\ell]\ g(s^2/2)$$

and

$$C'_u = \text{upper limit} = \exp[C_u]\ g(s^2/2)$$

where

$g(t)$ is the series given in Section 6.2

To obtain 95 percent confidence limits for the emission factors, the confidence limits for the percent leaking and for the mean leak rate were combined as follows:

lower 95% limit for emission factor = $P_{\ell}\ (C'_{\ell})$

upper 95% limit for emission factor = $P_{u}\ (C'_{u})$

These confidence intervals are conservative in the sense that 95 percent is a lower bound for the confidence coefficient for the intervals. The confidence intervals should be interpreted as follows:

> When we state that the true emission factor falls within the limits computed as described above, we expect to be correct at least 95 percent of the time.

These confidence intervals consider random sampling variation and random test error, with no adjustments for potential bias in the sampling and analytical methods. The potential sources for bias have been discussed in previous sections of the appendix:

- recoveries from sampling,
- analytical inaccuracies,
- biases in estimating leak rates from nonsampled sources, and
- bias in assuming sources screening < 200 could be considered as zero leak rates.

Sections 2.1 and 2.3 of this appendix discussed potential biases from sampling and analysis. It was concluded that there was no evidence of bias in the final leak rate data except for Refinery "F" where a low bias of about 15 percent was indicated. Based on the percent of sampled sources from

Refinery "F," the estimated total effect of this bias was as follows:

Source Type	Estimated Bias (%) In Emission Factor
Valves	- 1.8
Pump Seals	- 2.0
Flanges	- 0.7
Compressor Seals	- 0.3
Relief Valves	- 1.4
Drains	- 2.1

These biases were considered as systematic errors and therefore the emission factors and confidence limits were adjusted upward by the appropriate percentage as given above.

Potential biases from estimating leak rates from screening values were discussed in Section 6.1. Estimates of negative and positive potential biases were given. To account for this potential bias, lower confidence limits were adjusted downward by the appropriate percentage for positive bias and upper confidence limits were adjusted upward by the negative potential bias estimate.

Only for flanges did the assumption of zero leak rates for sources with screening values less than 200 ppmv appear to have a potential impact on the emission factor estimate. This was discussed in Section 6.2. To account for this potential bias, the upper confidence limit for the flange emission factor estimate was increased by 93 percent.

The systematic errors discussed above were considered independent so the net effect of combining all types of systematic errors was used in adjusting the emission factors and confidence limits. The following table summarizes these net systematic adjustments made tc emission factors and confidence intervals:

Source Type	Total Systematic Adjustments (%)		
	Lower Confidence Limit	Upper Confidence Limit	Emission Factor Estimate
Valves	- 0.6	+ 2.7	+ 1.8
Pump Seals	- 0.9	+ 4.7	+ 2.0
Flanges	+ 0.4	+ 93.6	+ 0.7
Compressor Seals:			
Hydrocarbon	- 13.8	+ 12.1	+ 0.3
Hydrogen	- 2.9	+ 1.9	+ 0.3
Relief Valves	- 4.6	+ 6.5	+ 1.4
Drains	- 2.1	+ 5.6	+ 2.1

6.4 Development of Nomographs

Three types of nomographs were developed as part of the statistical analyses for this project:

- predicting mean leak rate from screening values,
- cumulative distribution of sources by screening values, and

- cumulative distribution of total emissions by screening values.

This section describes how these nomographs were constructed.

6.4.1 Predicting Mean Leak Rate from Screening Values

Section 6.1 describes least-square linear regression equations developed for predicting leaks from nonsampled sources in the data base with screening values greater than 200 ppmv. For prediction purposes outside the data base, a statistical analysis of covariance was done to determine if different equations were required for the various source types and stream groupings. The data used to develop these relationships and the resulting nomograph are given in Appendix B, "Detailed Results." Although the equations were developed on a logarithmic scale, the nomographs are shown on an arithmetic scale for ease in reading and interpolation. Predicting the arithmetic mean leak rate for a given screening value is similar to predicting the mean from a lognormal distribution as discussed in Section 6.2. The mean value for a given screening value on the nomograph was computed as follows:

$$\text{mean} = \exp_{10}[B_0 + B_1 \log_{10}(\text{screening})]\ g(SE^2_{\ell n}/2)$$

$$= (10)^{B_0}(\text{screening value})^{B_1}\ (\text{scale bias correction factor})$$

where

B_0 = log regression intercept

B_1 = log regression slope

$SE_{\ell n}$ = standard error of estimate in natural log scale

g(t) = series described in Section 6.2.

The 90 percent confidence intervals for the predicted mean leak for a given screening value were computed in a similar manner to the confidence intervals for the mean leak rate as described in Section 6.2.

6.4.2 Cumulative Distribution of Sources by Screening Values

Another set of nomographs included in Appendix B contains the estimated cumulative distribution of log screening values. The nomographs show 100 percent minus the cumulative percent, or the estimated percent of sources which would have screening values greater than any particular screening value. These cumulative distribution functions were estimated by fitting a lognormal distribution, as described in Section 6.2, to the screening data and then generating the cumulative distribution.

There was some difficulty in fitting the lognormal distribution to the screening values. Figure C6-13 shows a typical histogram of log screening values for valves in gas service. The histogram appears to approximate a normal distribution adequately up to 10,000 ppm (4.0 on $\log_{10}$ scale). The spike at 10,000 ppm was due to the inability of the screening device to measure beyond 10,000 without a dilution probe. The dilution probe was used in only a few cases in the screening process during this program. The dilution probe was used for rescreening in all refineries except the first three

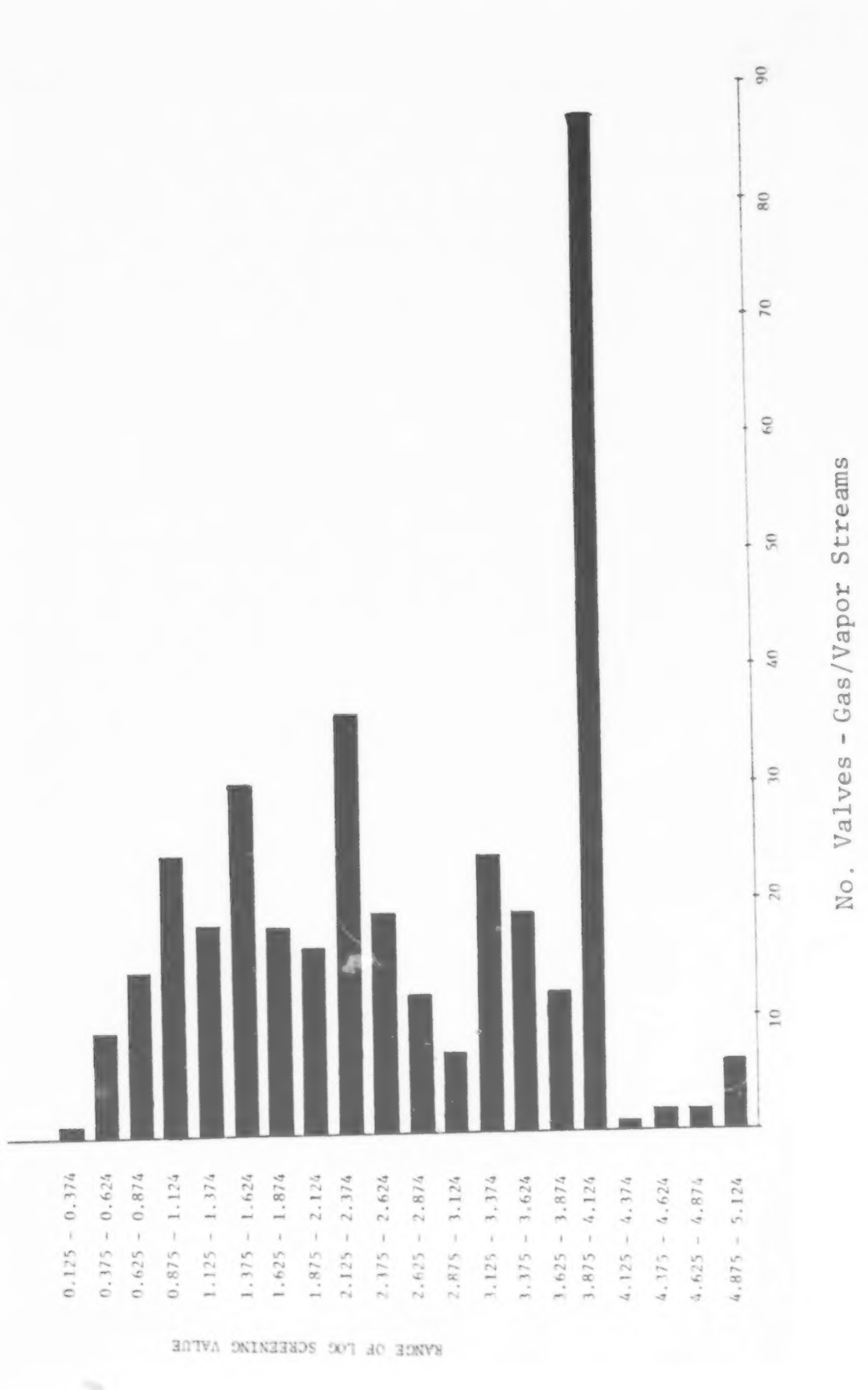


FIGURE C6-13. Distribution of Log_{10} (MAX Screening Value)

visited. However, the original screening values were required for the analysis.

To overcome the bias caused by this spike, only log screening values less than 4.0 were used to estimate the parameters of this distribution. Formulas from "censored" normal distribution theory (Cohen,[2] 1959) were then used to arrive at unbiased estimates of the entire distribution. These estimates were used to generate the cumulative distribution function for each source type/process stream grouping.

Confidence intervals for these cumulative functions were obtained using the Binomial Distribution as in Section 6.3. The 95 percent confidence interval for individual probabilities were approximated using

$$\hat{p} \pm 1.96\,[\hat{p}(1-\hat{p})/n]^{1/2}$$

where $\hat{p}$ is the estimated cumulative percent and n is the number of screening values for each particular source type and stream group.

Assuming that the sources screened approximate a random sample from the population of a particular source type, these confidence intervals can be interpreted as follows:

> When we state that the true percent of sources in the population which have screening values greater than any selected screening value lies within the confidence bounds, we expect to be correct about 95 percent of the time.

Note that these limits apply to the entire population for a source type and are not necessarily applicable when addressing a particular situation concerning a small number (less than 100) of sources.

The estimated cumulative distribution functions were compared with the sample distribution function and appeared to fit the data for each case except compressor seals. Figures C6-14 through C6-22 show the estimated and sample distribution for the source types and important stream classifications. Discrepancies were found at the 10,000 ppmv screening value (4.0 log screening value) in almost all cases, but this was to be expected since the sample function had a big jump at this point.

For compressor seals, censoring the data at 10,000 ppmv eliminated 64 percent of the observations, so the log-normal parameters were reestimated using all the data as recorded. These estimates resulted in a "better" agreement between the sample and estimates distribution function, and were therefore used to generate the cumulative distribution function for compressor seals in both types of service.

6.4.3 Cumulative Distribution of Total Emissions by Screening Values

A third set of nomographs given in Appendix B, "Detailed Results," contains a function estimating the cumulative percent of the total emissions attributable to each particular source type/stream group as a function of increasing log screening values. As before, 100 percent minus the cumulative function is shown so that the percent of total emissions

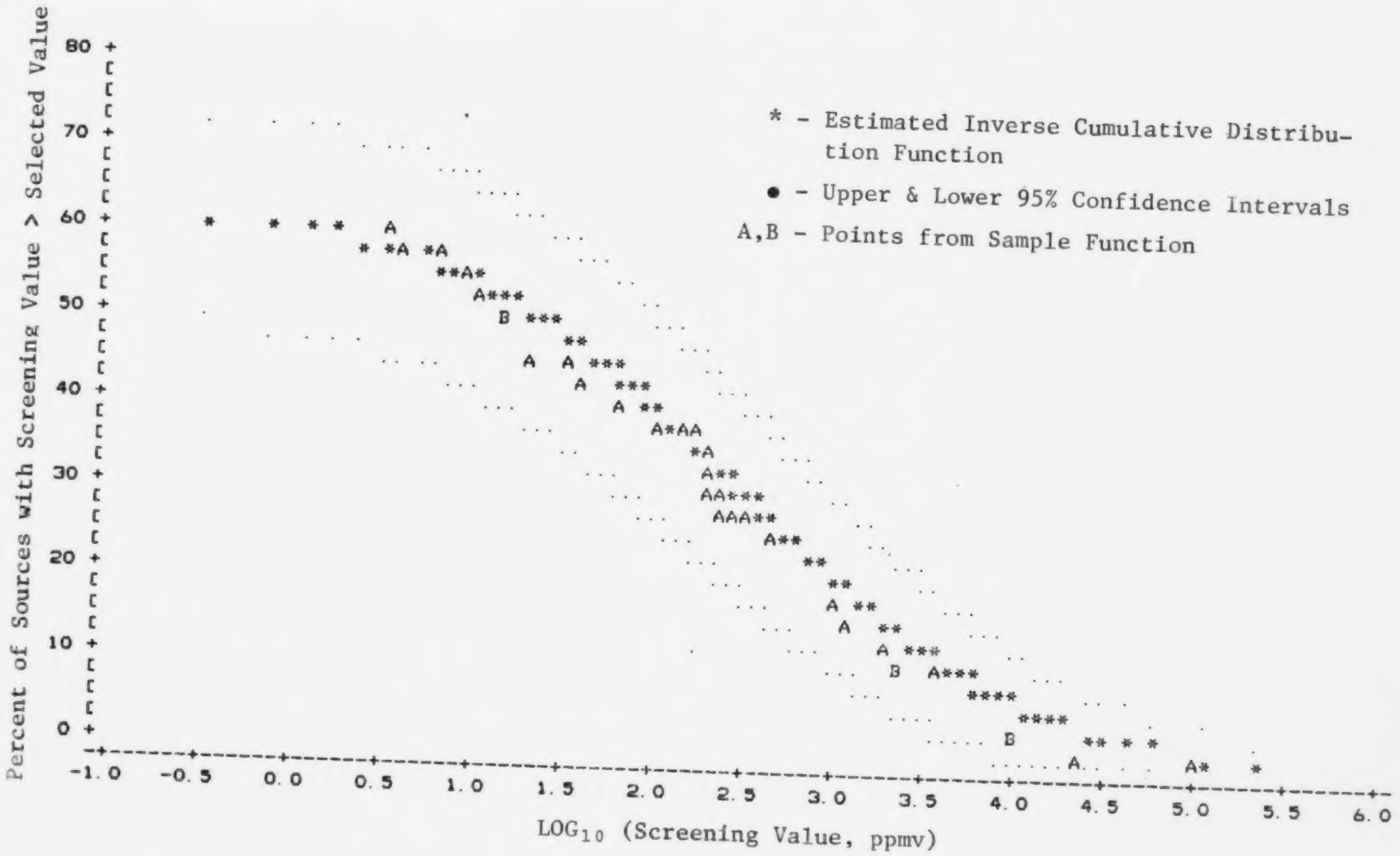


Figure C6-14. Inverse Cumulative Distribution Function for Relief Valves

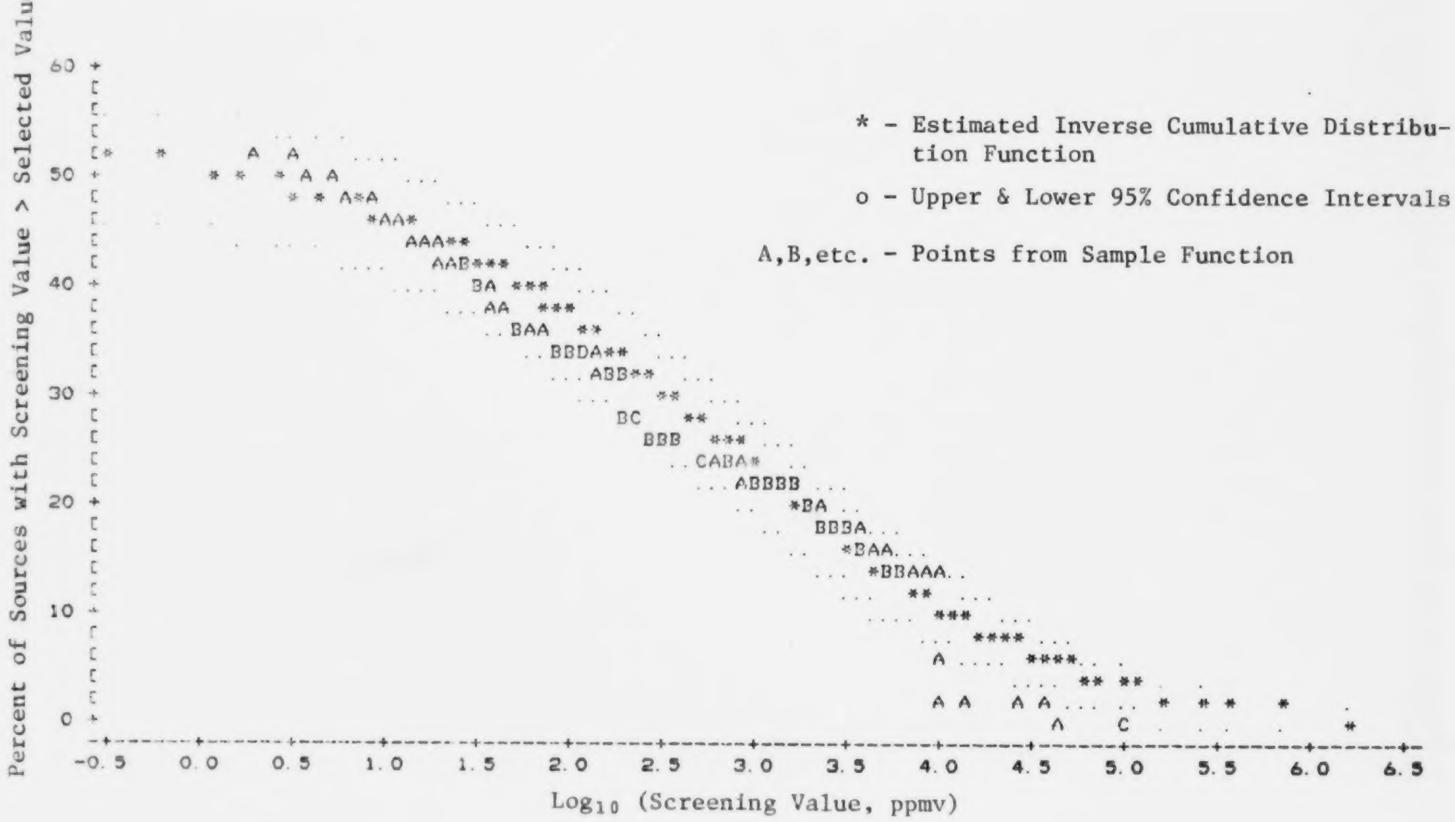


Figure C6-15. Inverse Cumulative Distribution Function for Valves, Gas/Vapor Streams

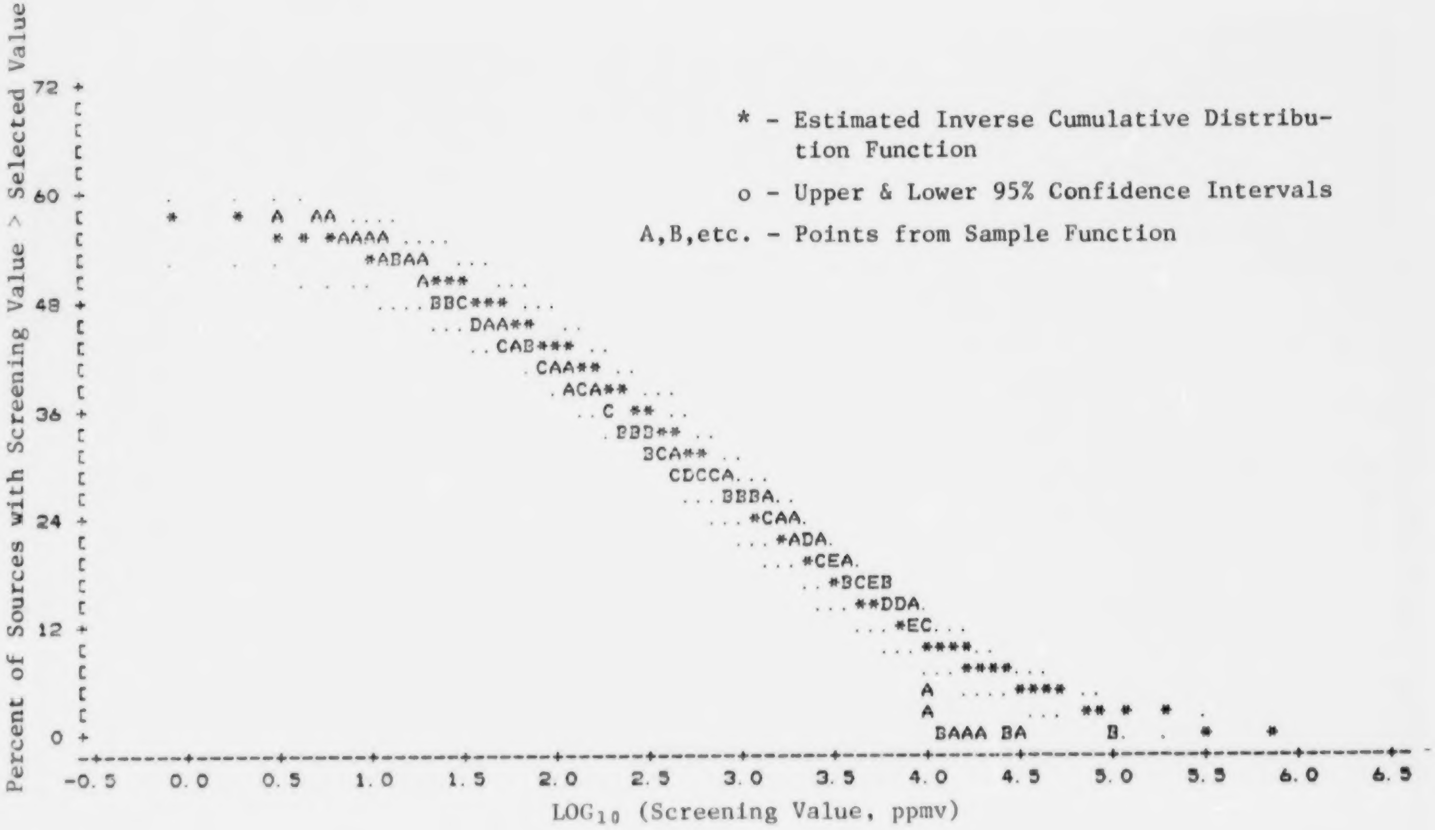


Figure C6-16. Inverse Cumulative Distribution Function for Valves, Light Liquid/Two-Phase

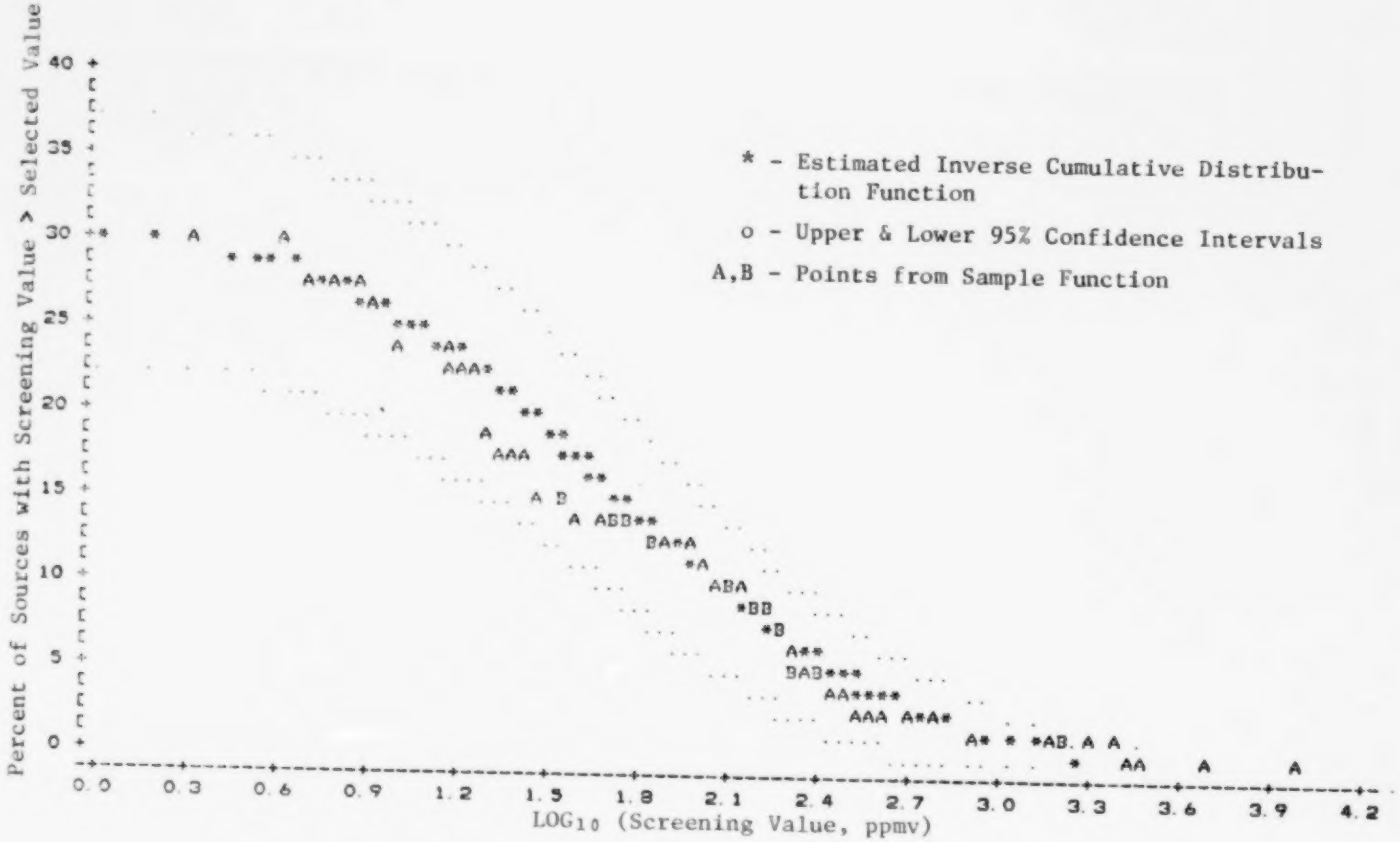


Figure C6-17. Inverse Cumulative Distribution Function for Valves, Heavy Liquid Streams

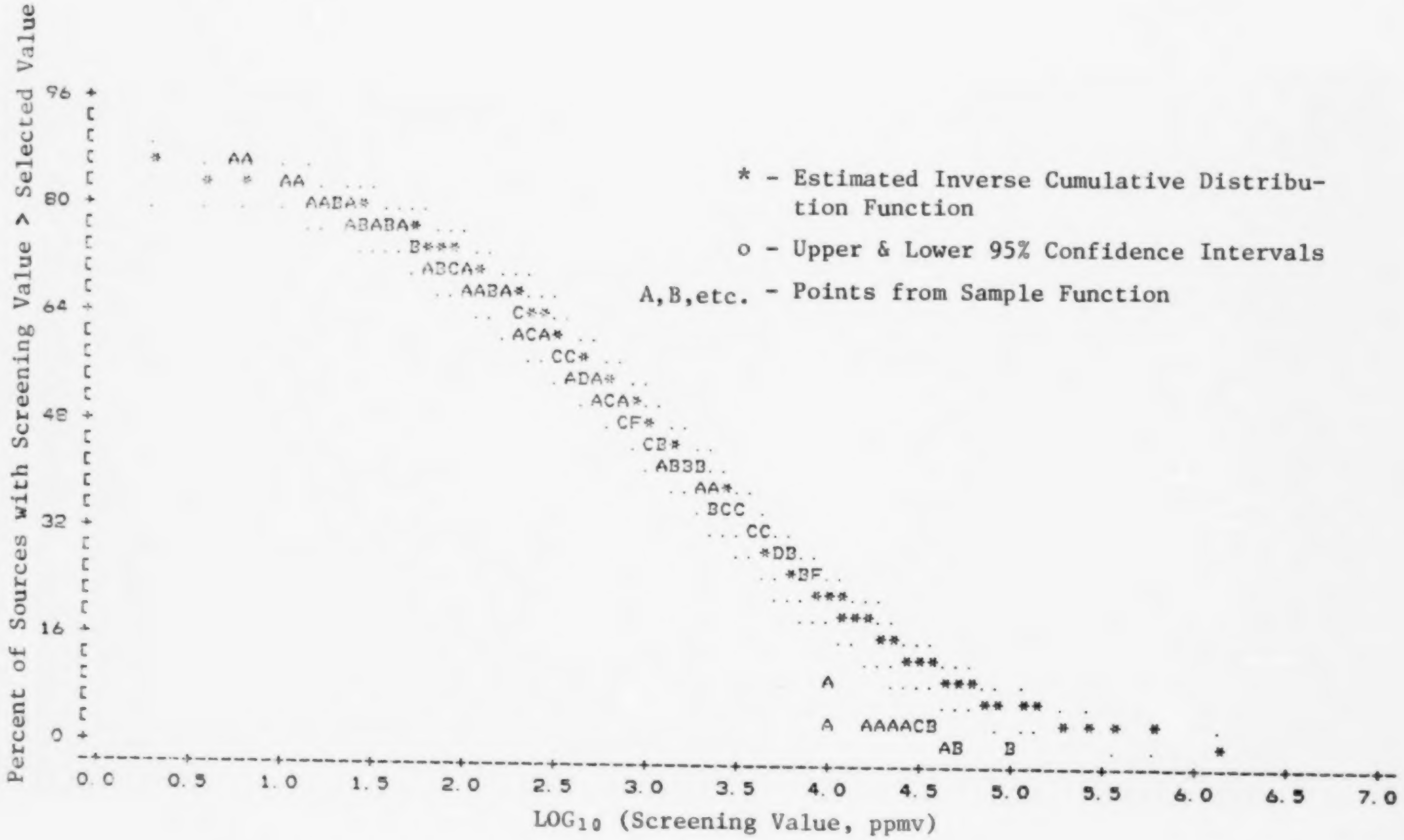


Figure C6-18. Inverse Cumulative Distribution Function for Pump Seals - Light Liquid Service

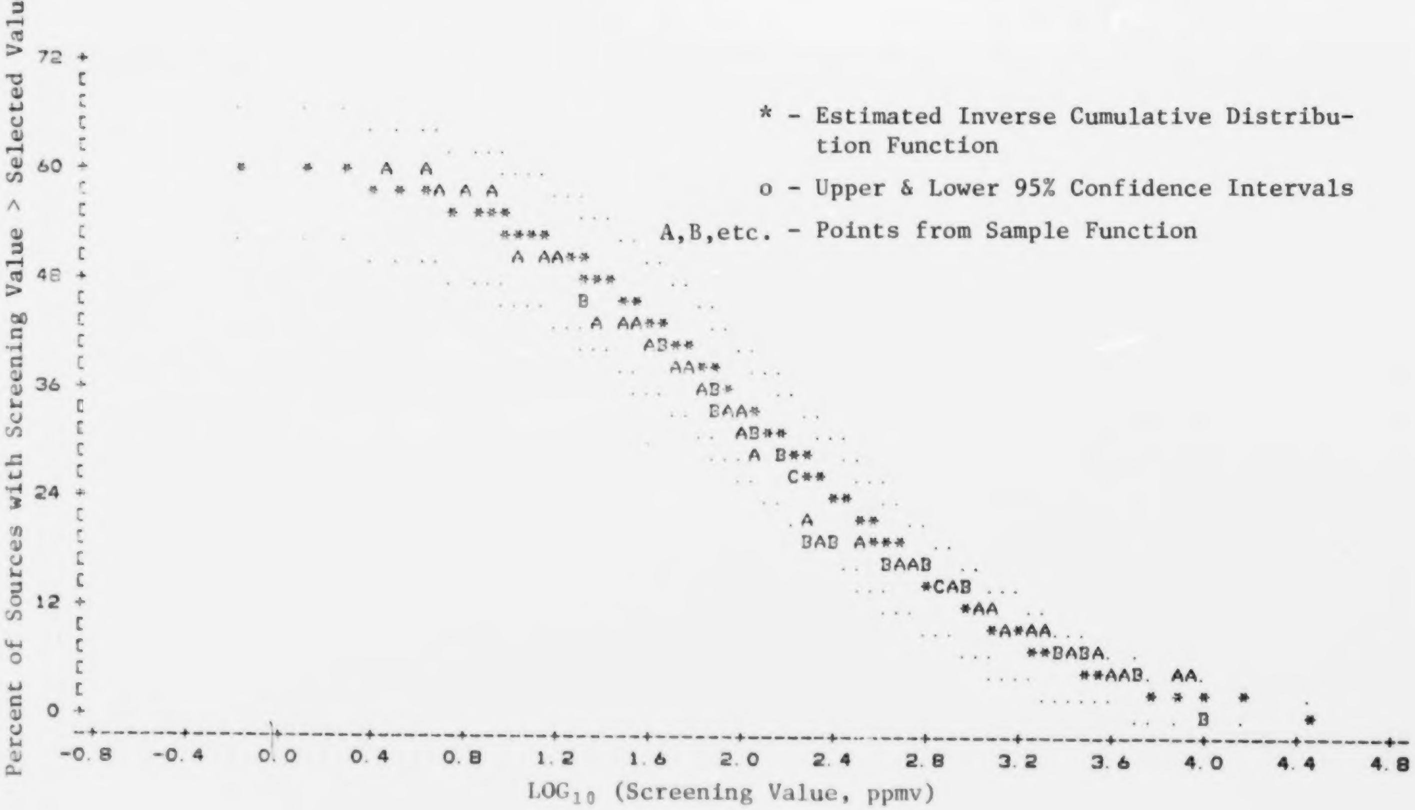


Figure C6-19. Inverse Cumulative Distribution Function for Pump Seals - Heavy Liquid Service

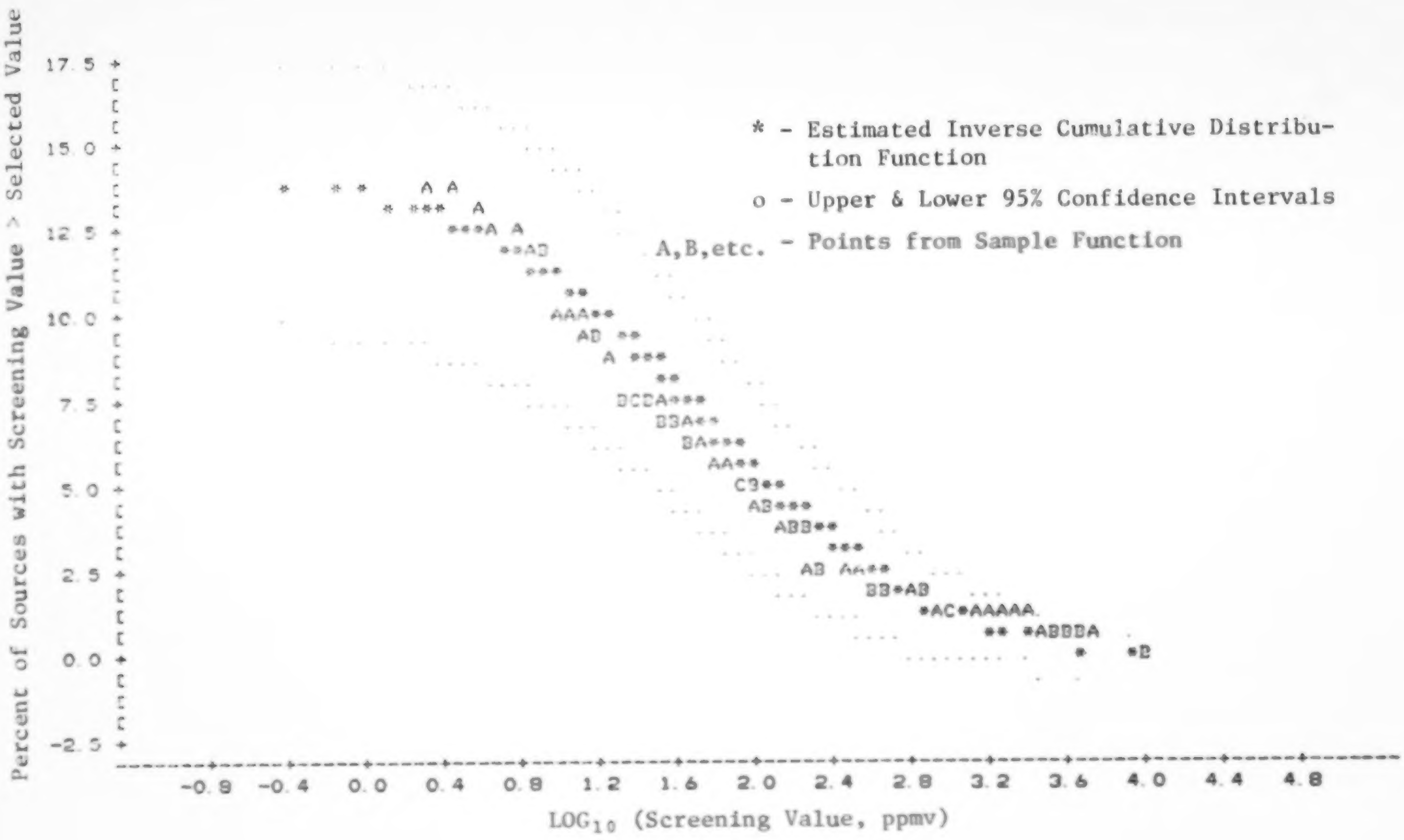


Figure C6-20. Inverse Cumulative Distribution Function for Flanges

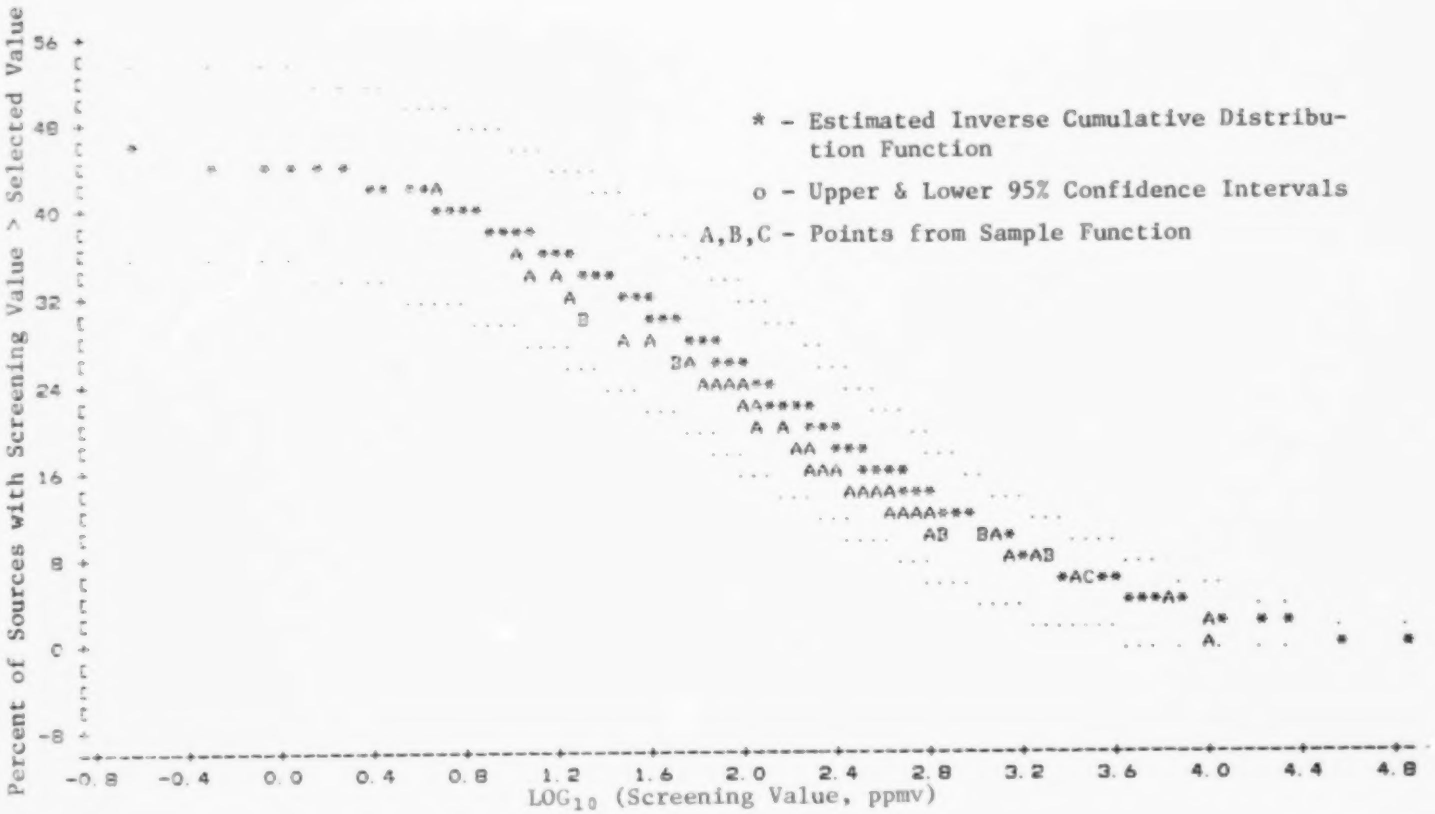


Figure C6-21. Inverse Cumulative Distribution Function for Drains

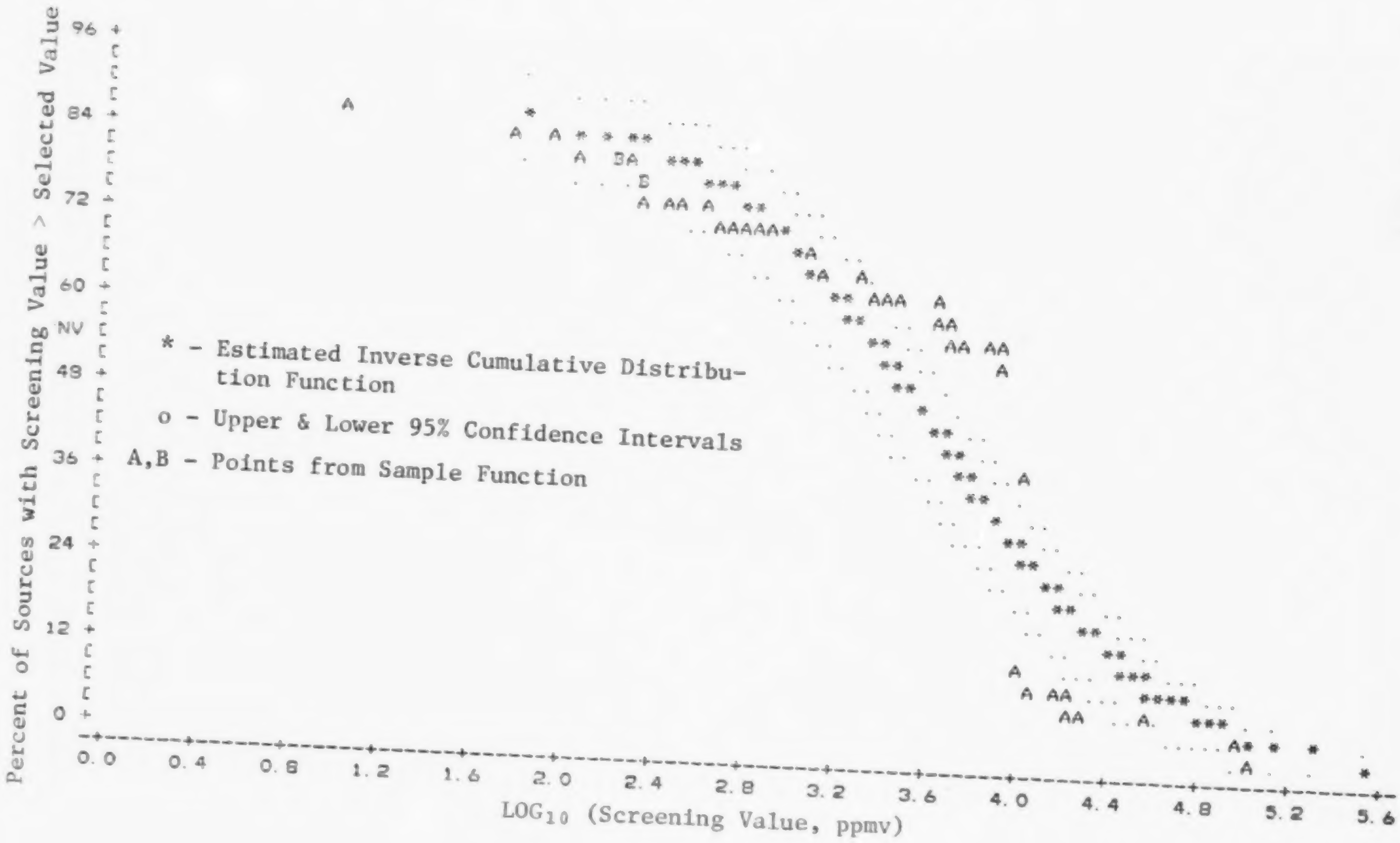


Figure C6-22. Inverse Cumulative Distribution Function for Compressor Seals

attributable to sources with screening values above any selected screening value can be determined.

This cumulative function was estimated by integrating the leak/screening regression relationship over a lognormal distribution of screening values. This function has the following form:

$$CF = \int_{0}^{S_o} \frac{C(10)^{B_o}(x)^{B_1}}{x\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ell n\ x - u)^2}{2\sigma^2}\right] dx \quad ,$$

where

S_o = selected upper screening value for integration,

C = log/arithmetic scale bias correction factor,

B_o = $\log_{10}$ regression intercept term,

B_1 = $\log_{10}$ regression slope term,

u = mean of the $\log_e$ (screening values),

σ^2 = variance of the $\log_e$ (screening values),

x = screening values over which the integration is being done, and

CF = cumulative function described above in lbs/hr.

The form of the cumulative function can be simplified by algebraic reduction and change of variables to obtain:

$$CF = C(10)^{B_0} \exp\left[- \frac{u^2 - (u + B_1\sigma^2)}{2\sigma^2}\right] \Phi \left[\frac{\ell n\ (S_0) - u - B_1\sigma^2}{\sigma}\right],$$

where Φ is the cumulative function of a standard normal distribution.

This function was used in developing the cumulative emissions function shown on the nomographs. The censored distribution parameter estimates described in Section 6.4.2 were used for the lognormal distribution parameters in each case except compressor seals. The log/log least-squares regression estimates described in Section 6.4.1 were used for the scale bias correction factor and for B_0 and B_1.

The scale for the above cumulative function is in lbs/hr. To obtain a cumulative percent function, the number obtained in lbs/hr at each screening value was divided by the value of the function at a screening value of one million ppmv. This forced the cumulative function to 1.0 at one million ppmv. These scaled values were then subtracted from 1.0 and multiplied by 100.0 to obtain the functions shown on the nomograph.

The estimated cumulative emissions functions were compared with the sample functions and found to adequately approximate the data in most cases. Figures C6-23 through C6-31 show the estimated and sampled functions for the source types and important stream classifications. Again, the biggest discrepancies were near the 10,000 ppmv screening value where the sample function has a big jump. This area is more critical for this function than the cumulative distribution function since most of the emissions are attributable to sources with screening values greater than 10,000 ppmv. It is important to

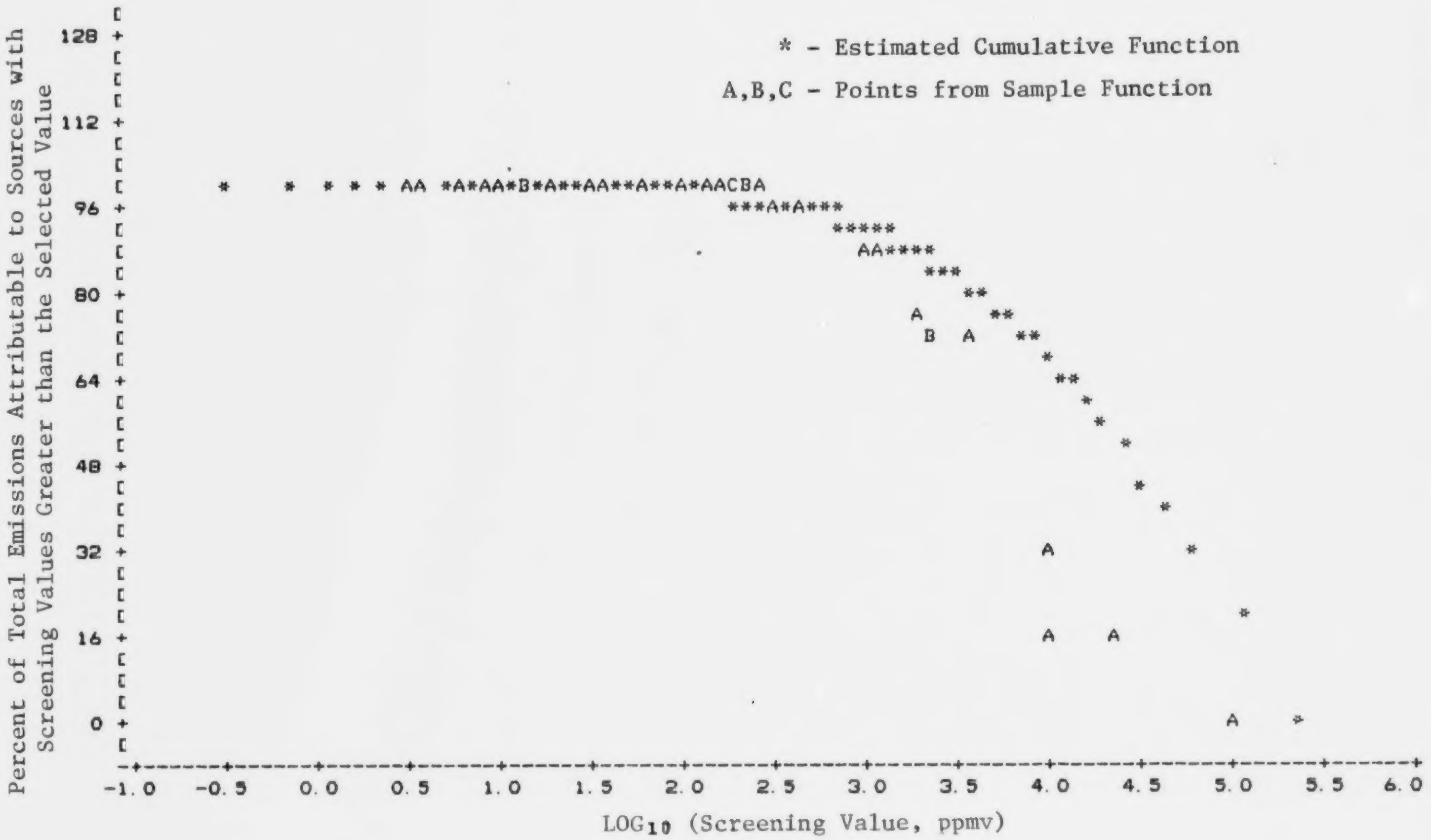


Figure C6-23. Cumulative Distribution of Total Emissions by Screening Values for Relief Valves

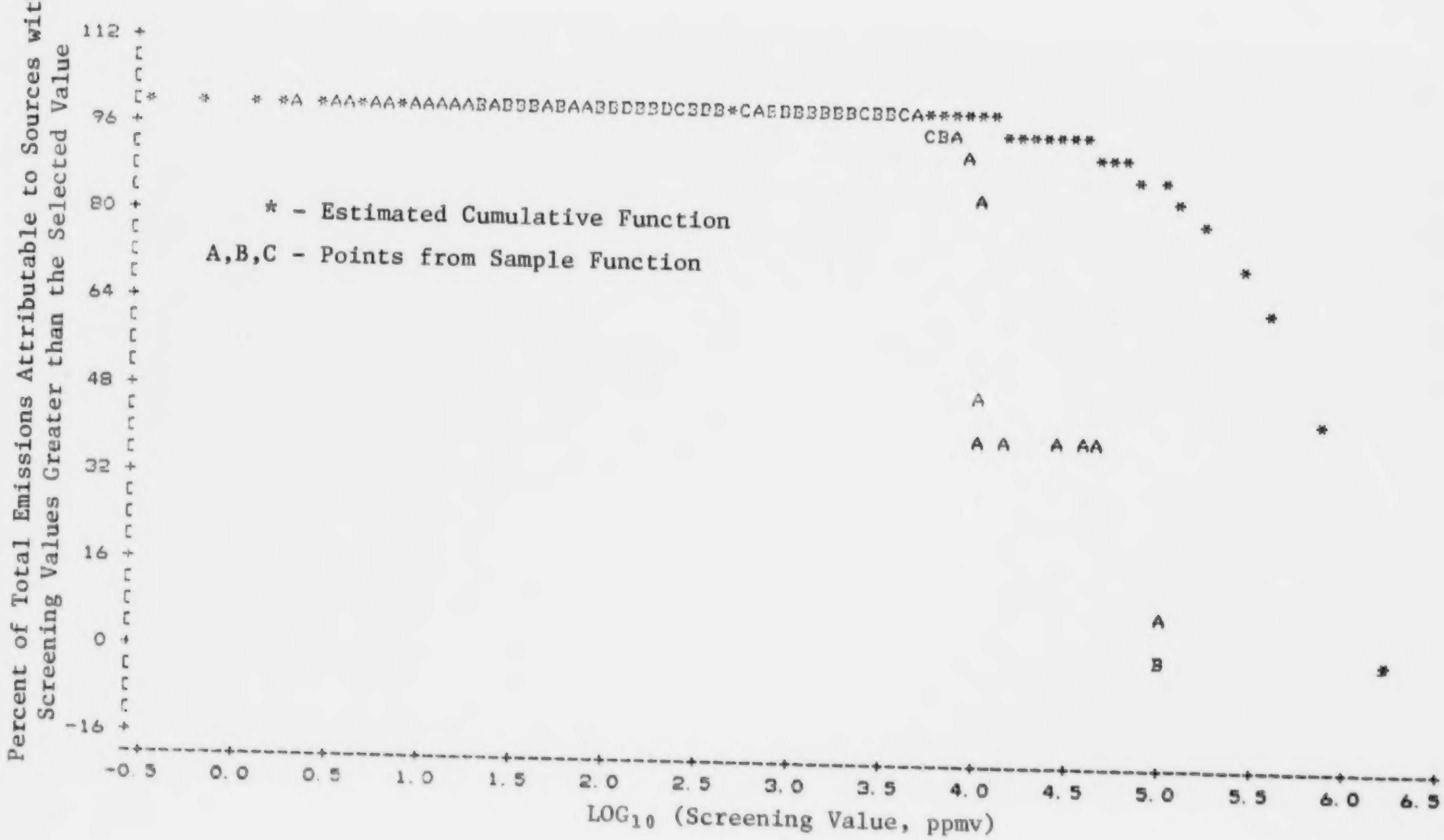


Figure C6-24. Cumulative Distribution of Total Emissions by Screening Values for Valves, Gas/Vapor Streams

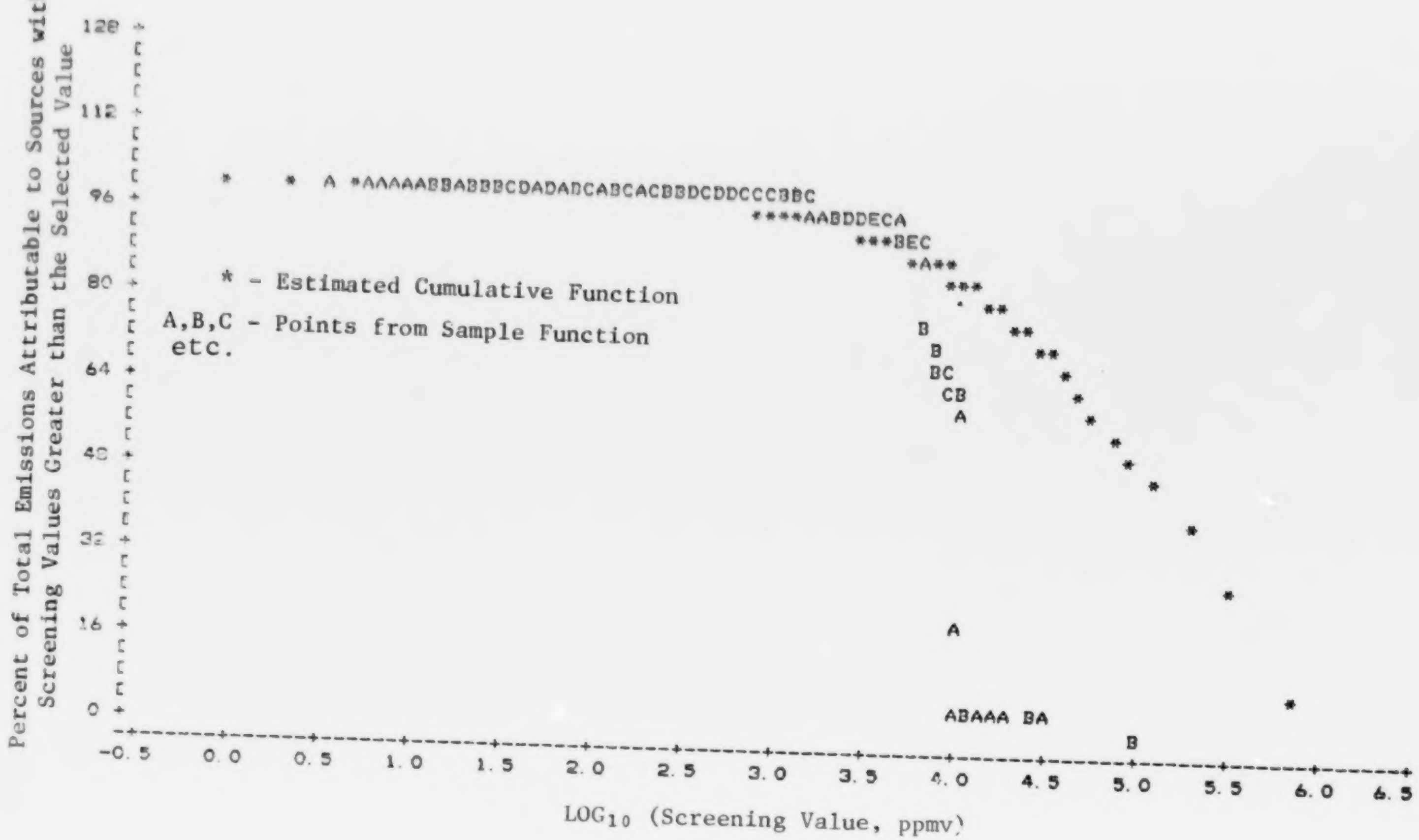


Figure C6-25. Cumulative Distribution of Total Emissions by Screening Values for Valves, Light Liquid/Two-Phase

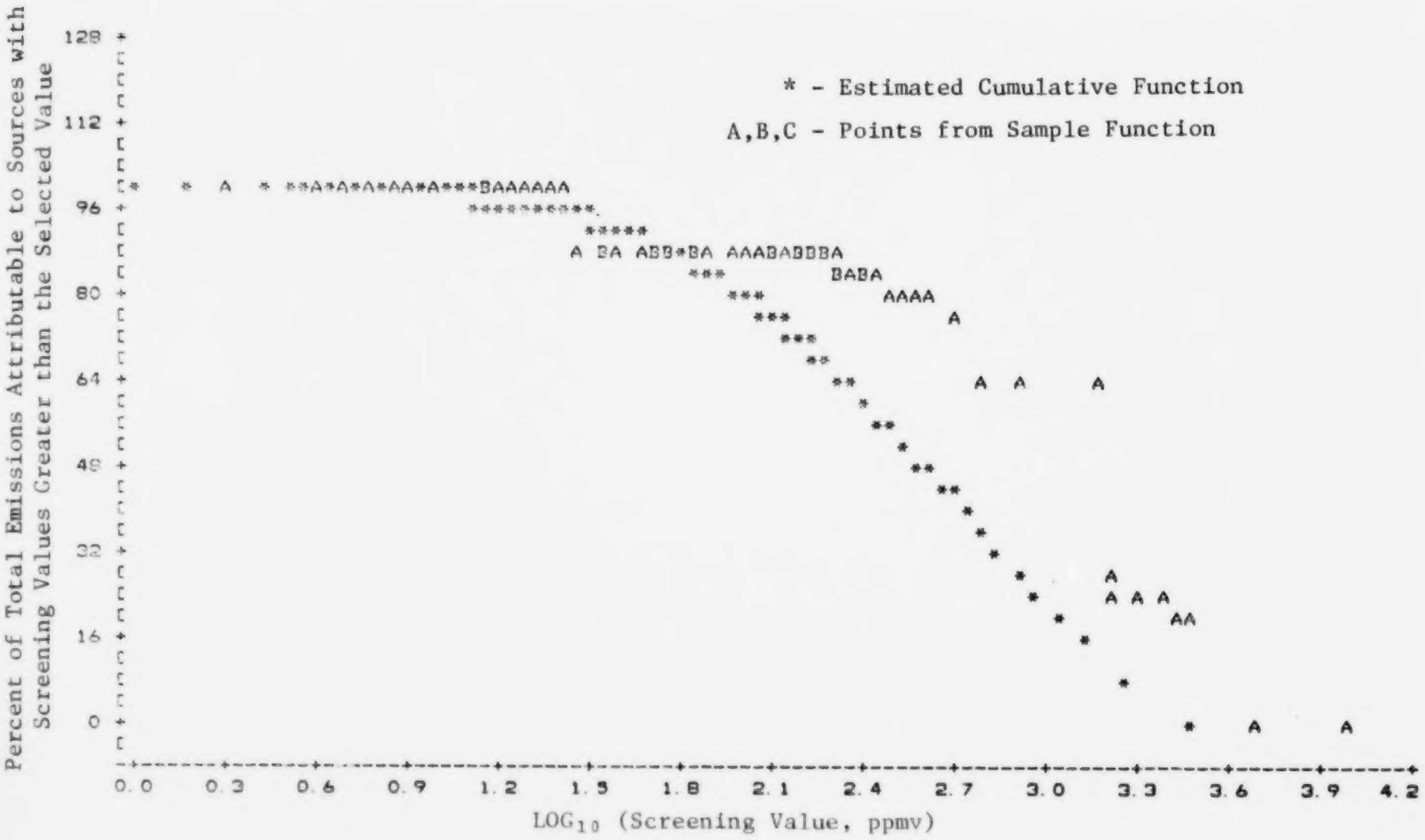


Figure C6-26. Cumulative Distribution of Total Emissions by Screening Values for Valves, Heavy Liquids

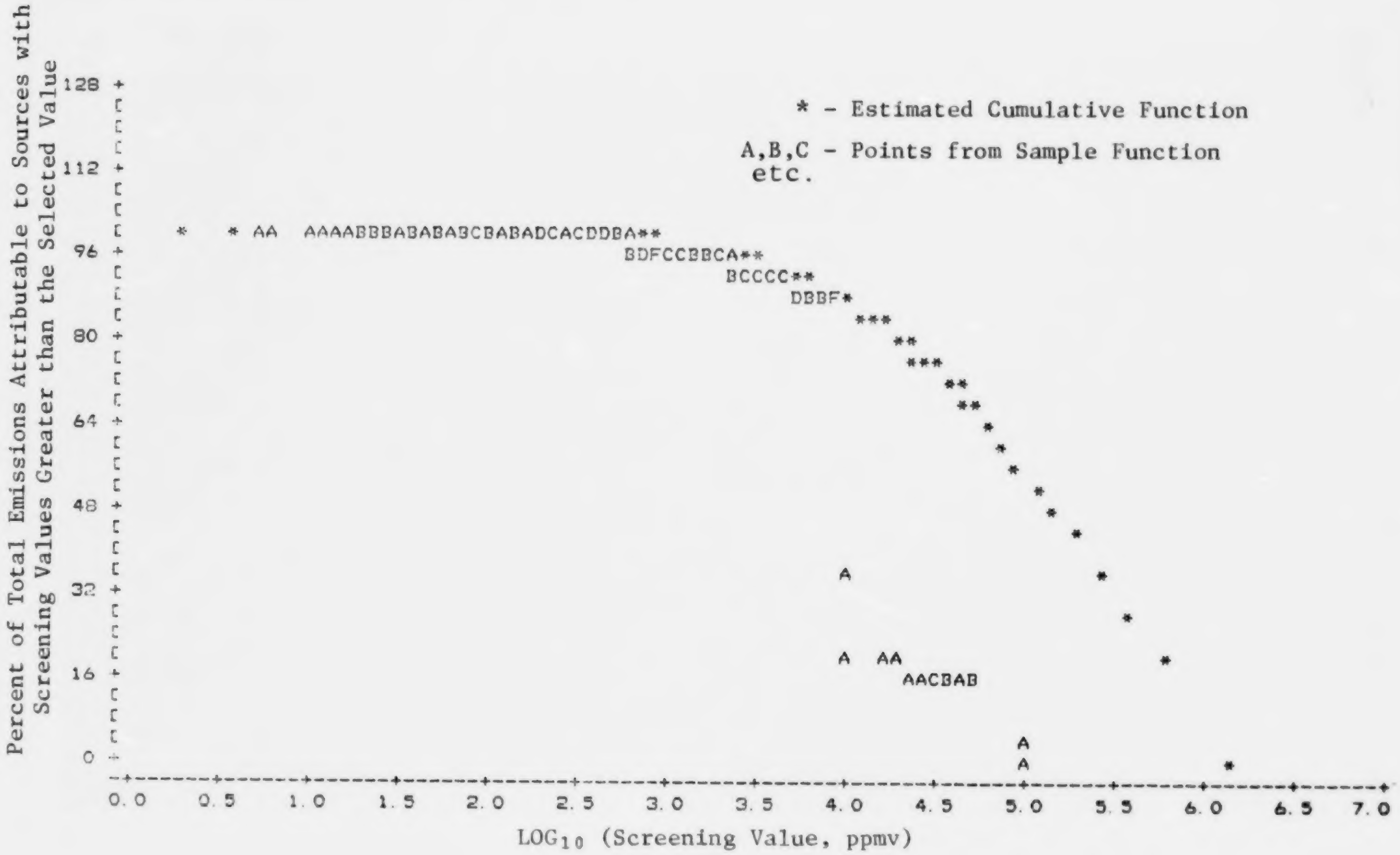


Figure C6-27. Cumulative Distribution of Total Emissions by Screening Values for Pump Seals, Light Liquid Service

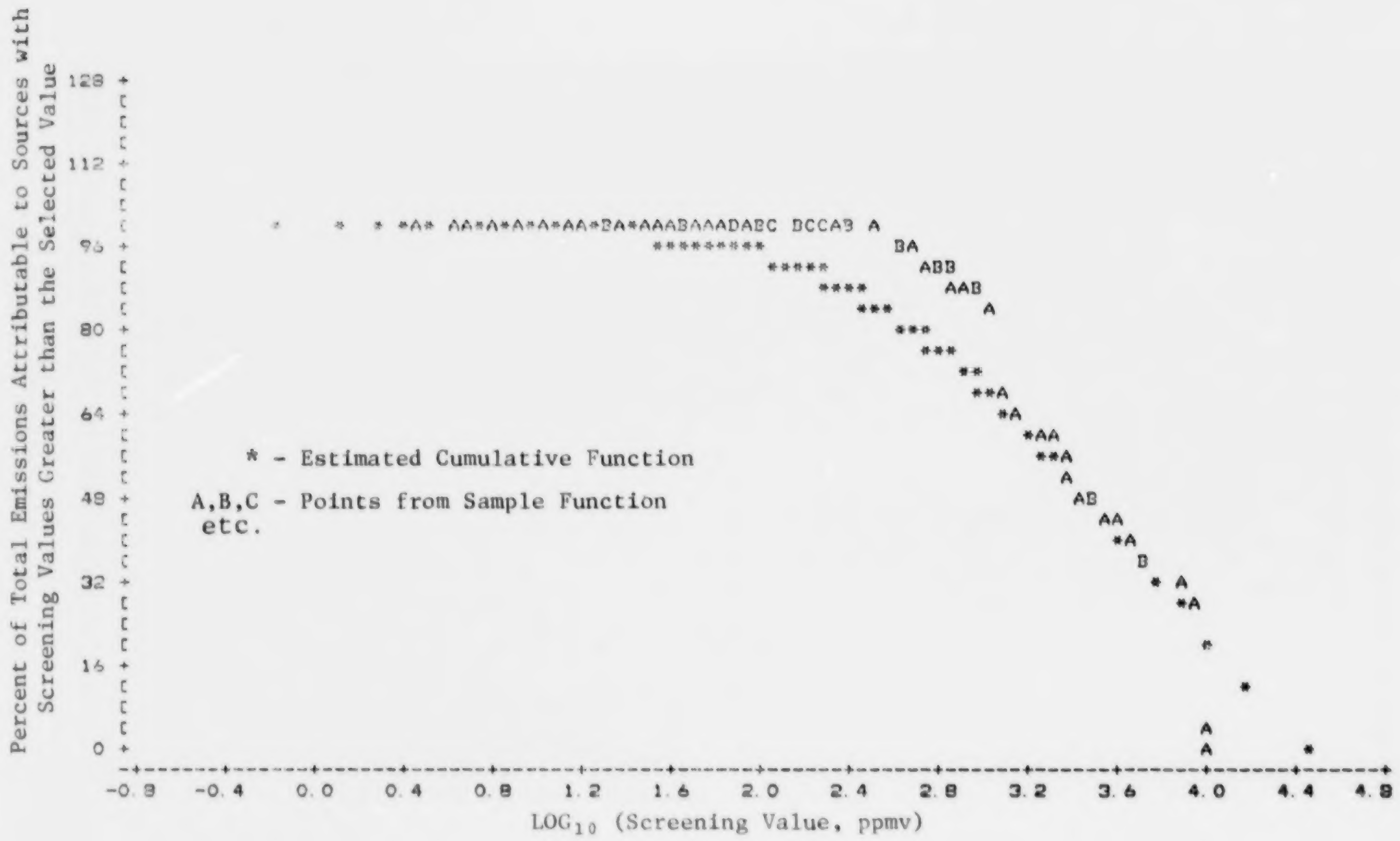


Figure C6-28. Cumulative Distribution of Total Emissions by Screening Values for Pump Seals, Heavy Liquid Service

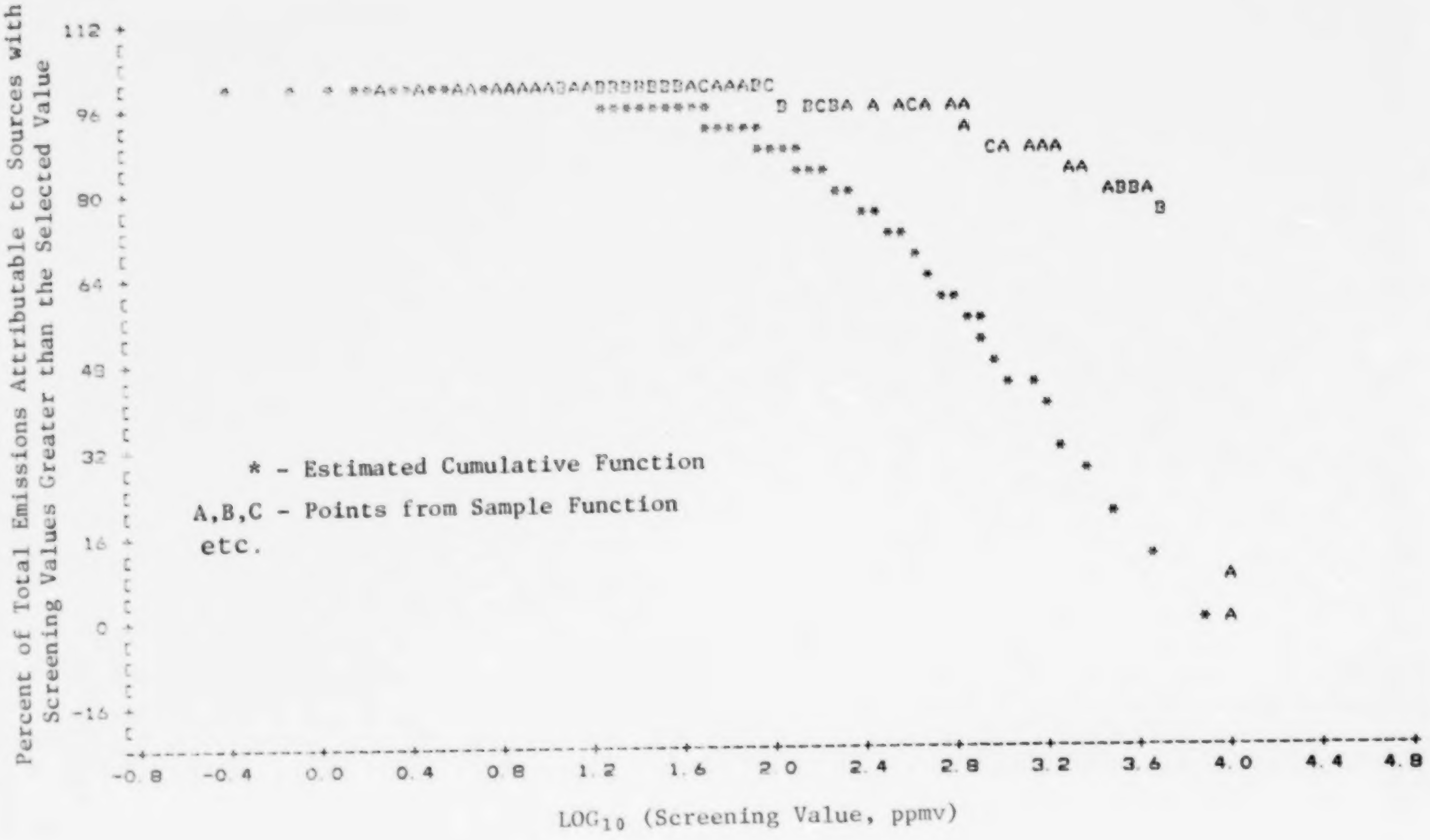


Figure C6-29. Cumulative Distribution of Total Emissions by Screening Values for Flanges

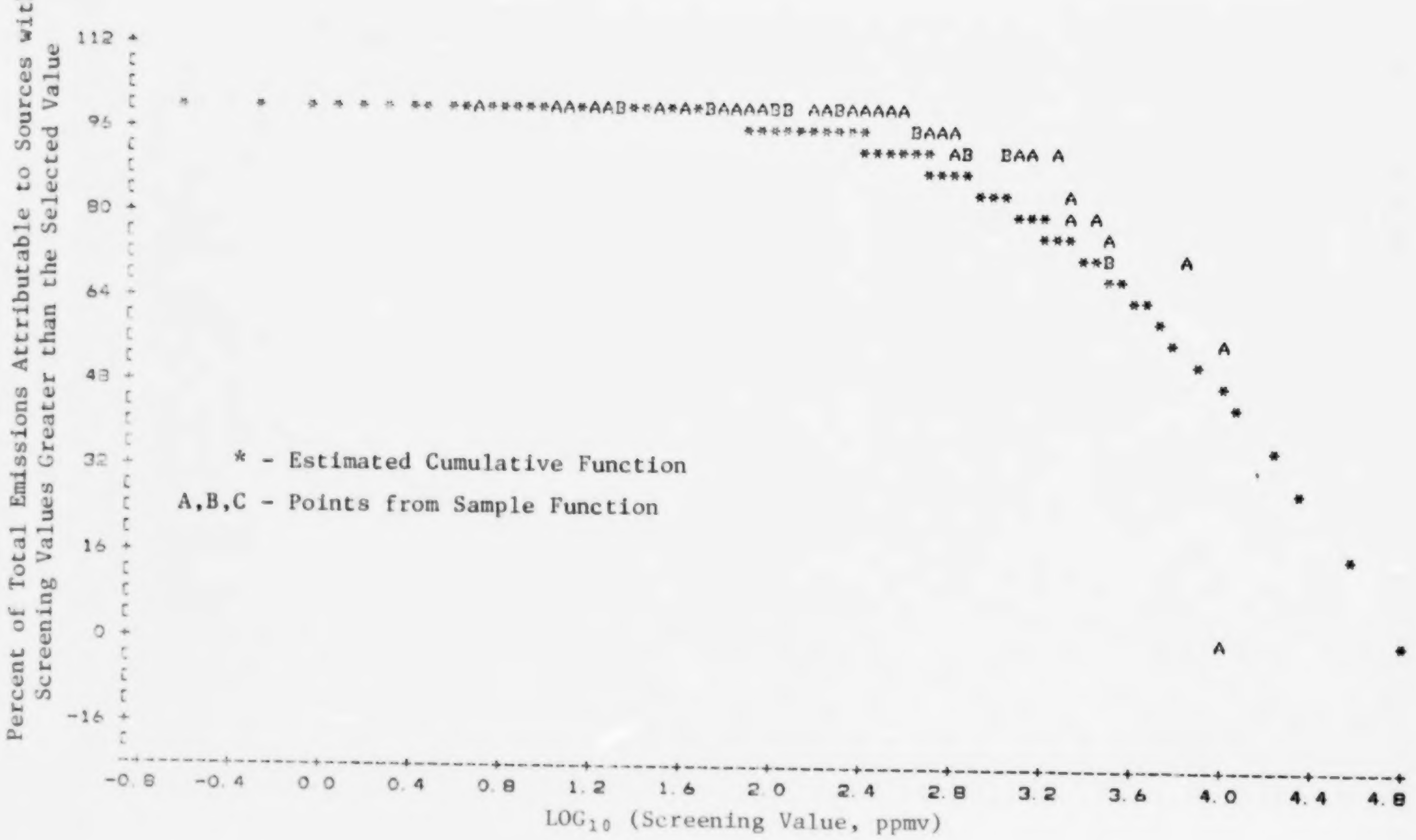


Figure C6-30. Cumulative Distribution of Total Emissions by Screening Values for Drains

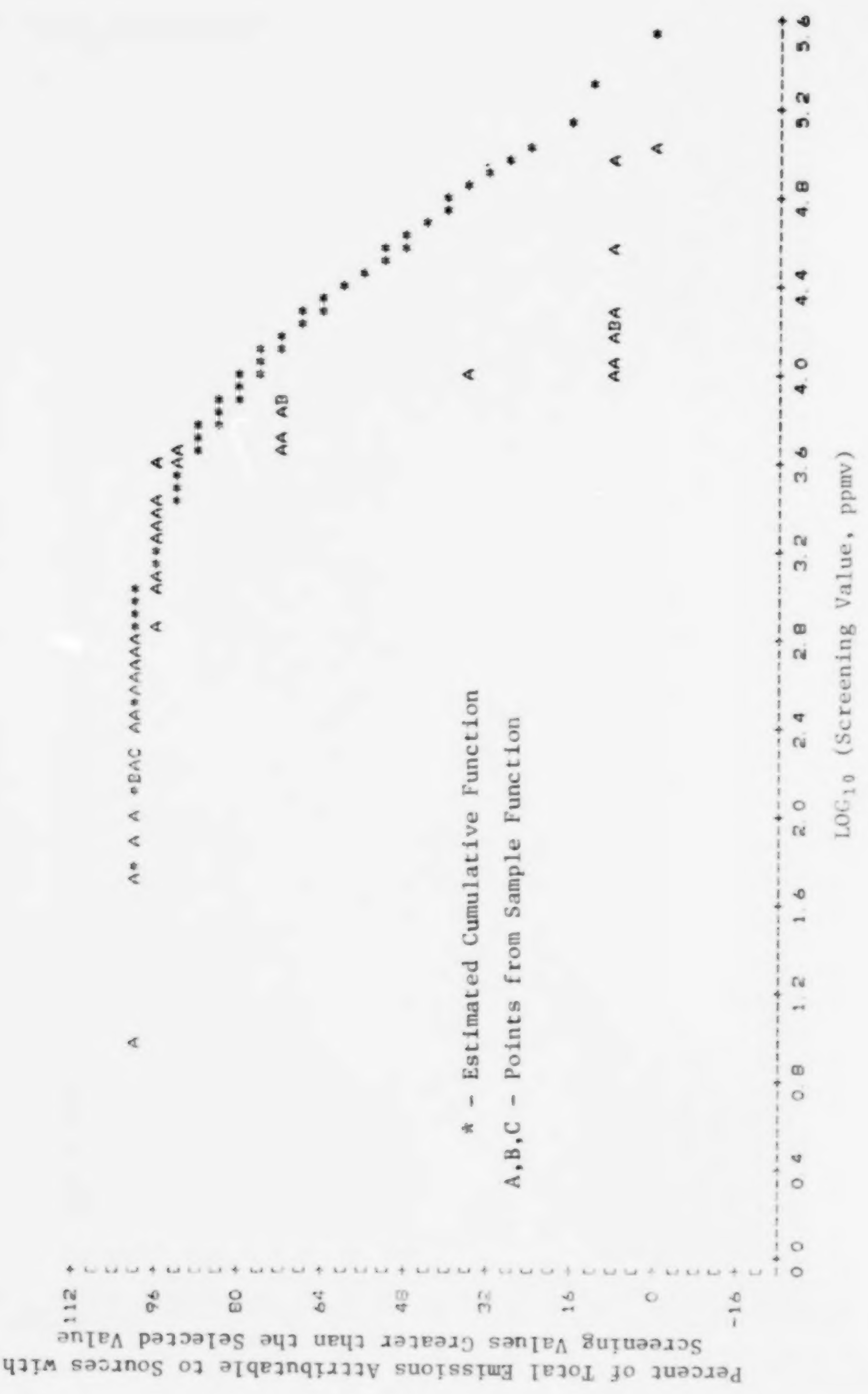


Figure C6-31. Cumulative Distribution of Total Emissions by Screening Values for Compressor Seals

note that very little screening data are available with screening values greater than 10,000 ppmv. Thus, this portion of the curve is based on extrapolations using models developed from screening values less than 10,000 ppmv.

This cumulative function is a very complex nonlinear function of five sample statistics:

- the intercept and slope from the regression of log leak rate on log screening value,
- a bias correction factor used when converting the logarithmic to the linear scale, and
- the mean and variance of the natural logarithm of the screening values.

Due to the complexity of this function, it was not possible to derive a closed-form analytical expression for the confidence intervals. Thus, a Monte-Carlo computer method was used to generate the confidence intervals.

This method involved regenerating the cumulative function 400 times. Each time, the data collected in the project (the number of sources with screening values greater than zero) were regenerated, except with an independent set of random variations. The distributional properties of the leak rate and screening data were used in computing the required random numbers.

For each of the 400 trials, sample estimates of the five parameters required to compute the cumulative function were computed. Then these estimates were used to generate a new cumulative function. The five percent lower result and the five percent upper result from the 400 trials for any given screening value were then selected as the 90 percent confidence limits for the population cumulative function. These approximated 90 percent confidence limits can be interpreted as follows:

> When we state that the true percent of total emissions for the population of sources, attributable to source with screening values greater than a selected value, is within the confidence bounds, we expect to be correct about 90 percent of the time.

Since these confidence limits address the uncertainty in the cumulative function for the entire sampled population of a particular souce type, they are not necessarily applicable to a finite sample of sources in a particular situation. The variation of this function depends on the number of sources in a complex manner, so it is not possible to draw a general conclusion for the effect of sample size. Monte-Carlo simulation techniques can be used to approximate intervals for a finite random sample of a particular source type.

As an example, Figure C6-32 shows the confidence intervals for the cumulative percent of emissions functions for valves in light/two-phase service. Intervals are shown which are applicable to a random sample of 100 valves and a random sample of 1,000 valves. Also included are the confidence intervals for the entire population. As can be seen,

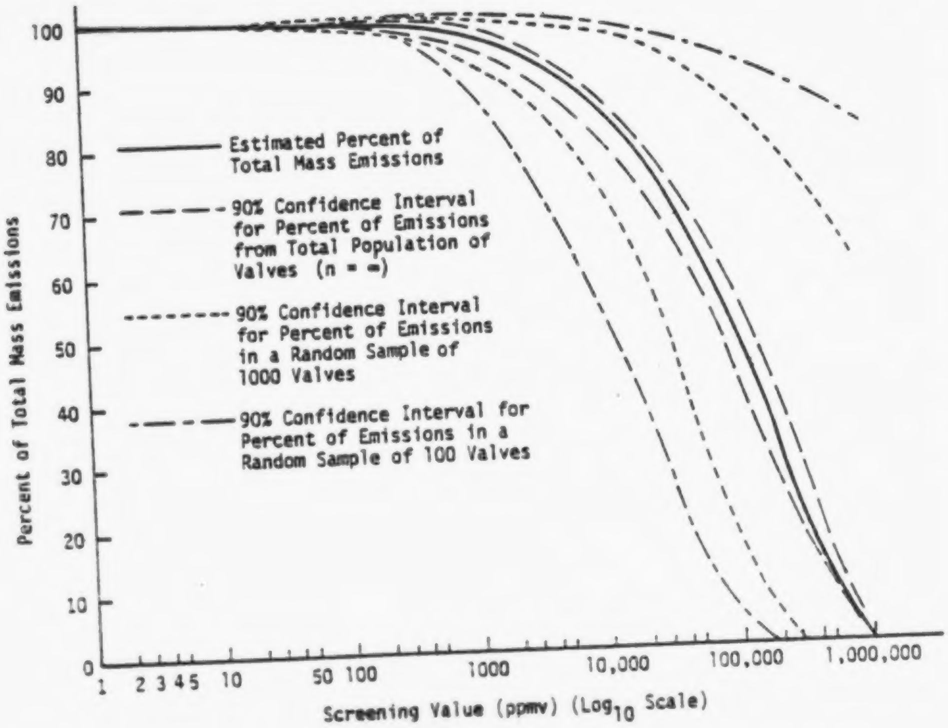


Figure C6-32. Cumulative Distribution of Total Emissions by Screening Values - Valves - Light Liquid/Two-Phase Streams - Comparison of Confidence Intervals

the intervals applicable to a finite number of sources are significantly wider than those for the population.

These intervals for finite populations were also developed using simulation techniques. Four hundred Monte-Carlo Trials generating 1,000 sets of data and then 100 sets of data were run. In each of the trials, the generated sample was ranked according to screening values and a sample cumulative leak rate function computed. Each sample function was scaled by dividing by the total leak rate generated. Then the five percent lower result and the five percent upper result from the 400 trials for any given screening value were selected as the 90 percent confidence bounds.

These confidence intervals can be interpreted as follows where "m" is the number of randomly selected sources in a particular situation:

> When we state that the cumulative percent of total emission function, which would be generated from a random sample of "m" sources, will fall within the confidence bounds, we expect to be correct about 90 percent of the time.

7.0 CONVERSION FACTORS

To Convert From	To	Multiply By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
$lb/10^6$ Btu	g/Mcal	18.0
$grain/ft^3$	g/m^3	2.29
$gal/10^6 ft^3$	$\ell/10^6 m^3$	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mb/ℓ	119.8

REFERENCES

1. Aitchison, J. On the Distribution of a Positive Random Variable Having a Discrete Probability Mass at the Origin. American Statistical Association Journal, 50(9):901-908, 1955.

2. Cohen, A. C., Jr. Simplified Estimators for the Normal Distribution When Samples are Singly Censored or Truncated. Technometrics 1:217-237, 1959.

3. Finney, D. J. On the Distribution of a Variate Whose Logarithm is Normally Distributed. Journal of the Royal Statistical Society, Series B, 7:155-161, 1941.

4. Patterson, R. L. Difficulties Involved in the Estimation of a Population Mean Using Transformed Sample Data. Technometrics 8(3):535-537, 1966.

5. Wetherold, R. G., and L. P. Provost. Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units. EPA-600/2-79-044, EPA Industrial Environmental Research Laboratory, Research Triangle Park, 1979.

6. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Environmental Protection Agency, Office of Air Programs, Research Triangle Park, N.C., March 1972.

APPENDIX D:

DETAILED ENVIRONMENTAL ASSESSMENT

APPENDIX D: DETAILED ENVIRONMENTAL ASSESSMENT

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1.0 INTRODUCTION

The environmental assessment presented here is a method of examining the potential effects of refinery emissions on the surrounding atmosphere. It will utilize the large volumes of emission rate data generated in this program to estimate ambient pollutant levels. It also attempts to examine the environmental and public health effects of the predicted pollutant concentrations. Finally, a brief survey of the effects of existing and potential regulatory policies and developing technology is presented.

The primary objective of the environmental assessment is to provide guidance in identifying potential problem areas. For instance, it can provide insight into which sources and which pollutants appear to pose potential hazards. The results are semi-quantitative in nature, which allows a relative ranking of such problem areas. This can help to focus attention on those areas needing further research. The environmental assessment is only a tool to aid in the relative evaluation of potential environmental impacts, not a method for making precise and accurate predictions of such impacts. The results should not be regarded as an absolute value which can be used to predict violations of standards, public health hazards, requirements for additional pollution control technology, or regulatory requirements.

This type of analysis is particularly important for refinery fugitive emissions, where hydrocarbons are the only significant pollutant species. The rationale behind controlling hydrocarbon emissions is based on two diverse effects: the formation of photochemical oxidants and the toxic effects of some hydrocarbon species. Only through atmospheric modeling (or the even more expensive ambient monitoring) can the latter effects be assessed.

The approach to the environmental assessment follows these steps:

- Define a hypothetical refinery.
- Estimate its emissions.
- Estimate ground level concentrations by atmospheric dispersion modeling.
- Compare those ground level concentrations to some acceptable concentration.

The parameter which is used to quantify environmental impacts is called source severity. This concept was developed by Monsanto Research Corporation under contract to the EPA.[1] A source severity factor is defined as the ratio of the maximum ground level concentration of a pollutant in a "standard receiving atmosphere" to the "acceptable pollutant concentration," as shown below:

$$S = \frac{\overline{X}_{max}}{F}$$

where:

S = the source severity factor,

$\overline{X}_{max}$ = the maximum ground level concentration of the pollutant, and

F = the acceptable pollutant concentration.

This acceptable concentration is derived from either National Ambient Air Quality Standards (NAAQS) or from Threshold Limit Values (TLV's). If the resulting ratio is greater than 1.0, then further emission reduction is probably needed. If the ratio is below about 0.01, then further control is probably not needed. Intermediate values are in a gray area where further emission reduction may or may not be needed.

2.0 DEFINITION OF THE HYPOTHETICAL REFINERY MODEL

The first step in the environmental assessment is the selection and definition of the model refinery. The requirements of this model refinery are much broader than most. Not only must the refinery processing be characterized, but also its physical configuration. There is ample documentation of the difficulties involved in trying to synthesize a "typical, representative refinery." Refineries are very diverse, and only a very rough approximation can be achieved with a single model. When size and layout are added to the model, the task is complicated further. Therefore, it should be noted throughout this discussion that this is not a model that attempts to represent the total industry, but rather a model of one hypothetical refinery that reflects the "real world" as much as possible.

The source for the model refinery is an EPA report prepared by Pacific Environmental Services (PES)[2] in which detailed descriptions of the processing and physical layouts of several types of refineries are provided. The large existing refinery was chosen as the model for this study because it appears to represent the worst case. It is difficult to determine exactly which model would pose the worst case, because of the diversity of effects between stack emission sources, process area fugitive sources, and wastewater related fugitive sources. A complex refinery will carry its processing further, resulting in the production of higher volumes of aromatic compounds which will often be separated into relatively pure streams. This increases the likelihood of the occurrence of localized high concentrations of some of the more hazardous materials. An existing refinery was chosen because a stage-wise growth pattern over many years is likely to result in a less organized layout than a new grass roots refinery. This could aggravate the impact of emissions by placing a large source near the boundary line rather than in a well-planned central processing area buffered by surrounding greenbelt. Thus, if the environmental assessment indicates minimal impacts for a large existing refinery, then smaller, less complex, and more efficient grass roots refineries would probably create a lesser impact.

2.1 Refinery Process Configuration

Figure D2-1 shows the basic processing configuration of the model refinery. This refinery processes 350,000 barrels per stream day (BPSD) of mixed crudes to produce a full range of low sulfur fuels and specialty products. All of the normal refinery unit operations are represented, including:

- Atmospheric and vacuum crude distillation.
- Extensive hydrotreating of all ranges of product streams (such as naphtha, middle distillate, gas oils, and resid).
- Catalytic reforming.
- Aromatics extraction and separation of BTX.
- Hydrogen manufacturing.
- Fluid catalytic cracking with electrostatic precipitator and CO boiler.
- Sulfuric acid alkylation.

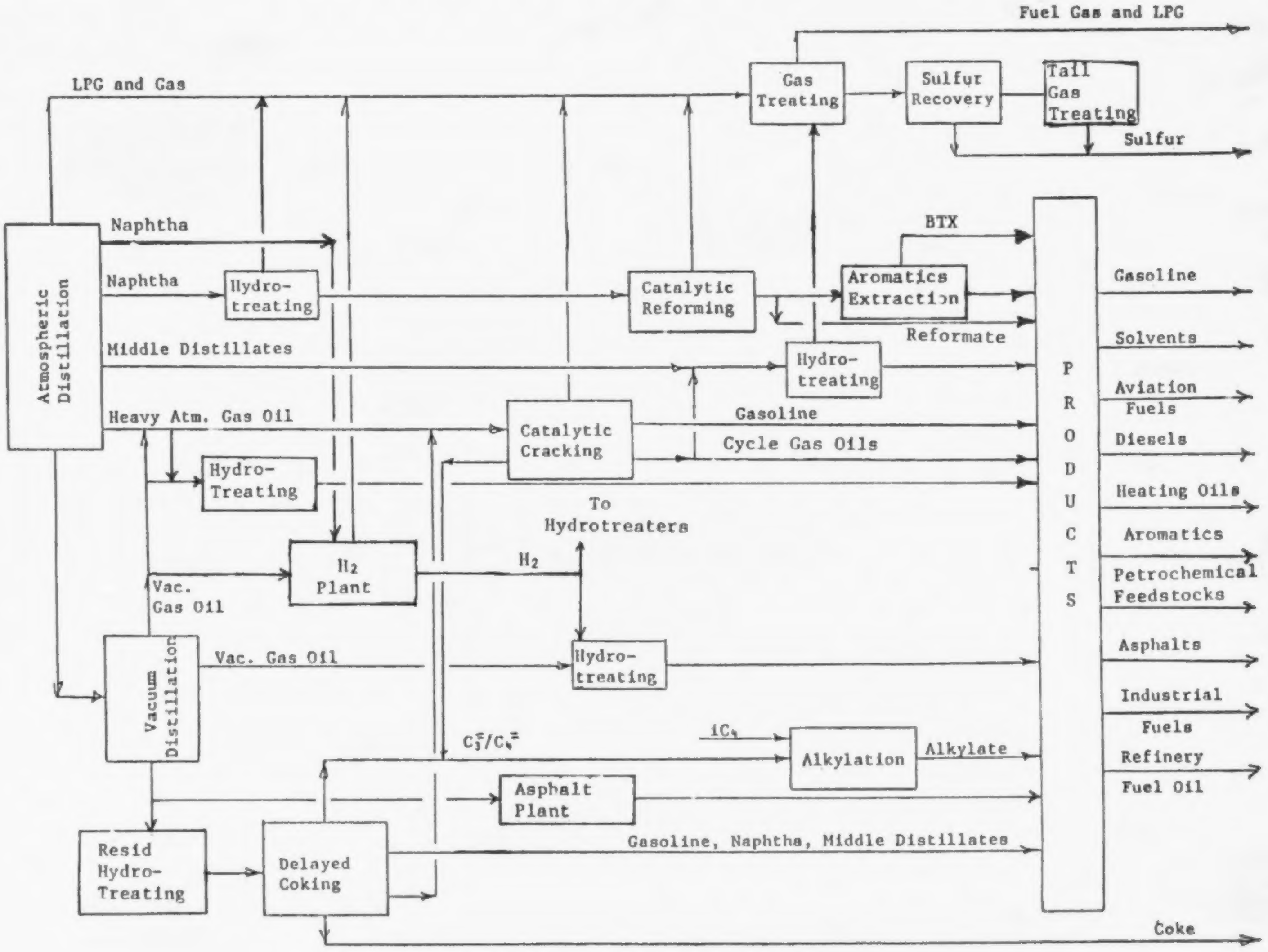
Fuel Gas and LPG
LPG and Gas
Gas Treating
Sulfur Recovery
Tail Gas Treating
Sulfur
Atmospheric Distillation
Naphtha
Naphtha
Hydro-treating
Catalytic Reforming
BTX
Aromatics Extraction
Reformate
Middle Distillates
Hydro-treating
Heavy Atm. Gas Oil
Catalytic Cracking
Gasoline
Cycle Gas Oils
Hydro-Treating
To Hydrotreaters
H_2 Plant
H_2
Vac. Gas Oil
Vacuum Distillation
Vac. Gas Oil
Hydro-treating
iC_4
$C_3^=/C_4^=$
Alkylation
Alkylate
Asphalt Plant
Resid Hydro-Treating
Delayed Coking
Gasoline, Naphtha, Middle Distillates
Coke
P R O D U C T S
Gasoline
Solvents
Aviation Fuels
Diesels
Heating Oils
Aromatics
Petrochemical Feedstocks
Asphalts
Industrial Fuels
Refinery Fuel Oil

Figure D2-1. Block flow diagram of model refinery.

- Claus sulfur recovery, Wellman-Lord tail gas treating, and a sulfuric acid plant.
- Gas processing (oil absorption/stripping and distillation).
- Delayed coker.
- Rerun stills for recovered oils.
- Many miscellaneous treating, brightening, etc., types of processing.

Again, it should be stressed that this configuration is not intended to represent the total industry. But is is a reasonable example of a modern refinery supplying low sulfur fuels and specialty products.

2.2 Refinery Layout

The plot plan of the refinery (shown in Figure D2-2) will give evidence of the detail which was presented in the PES report. The functions of the various refinery modules are detailed in Table D2-2. The process areas tend to form two clusters, probably the result of a stage-wise expansion. Considerable detail has been included in the physical model. All of the appropriate vital functions have been accounted for and distributed in a realistic manner. These are critical points in achieving meaningful results from the atmospheric dispersion model.

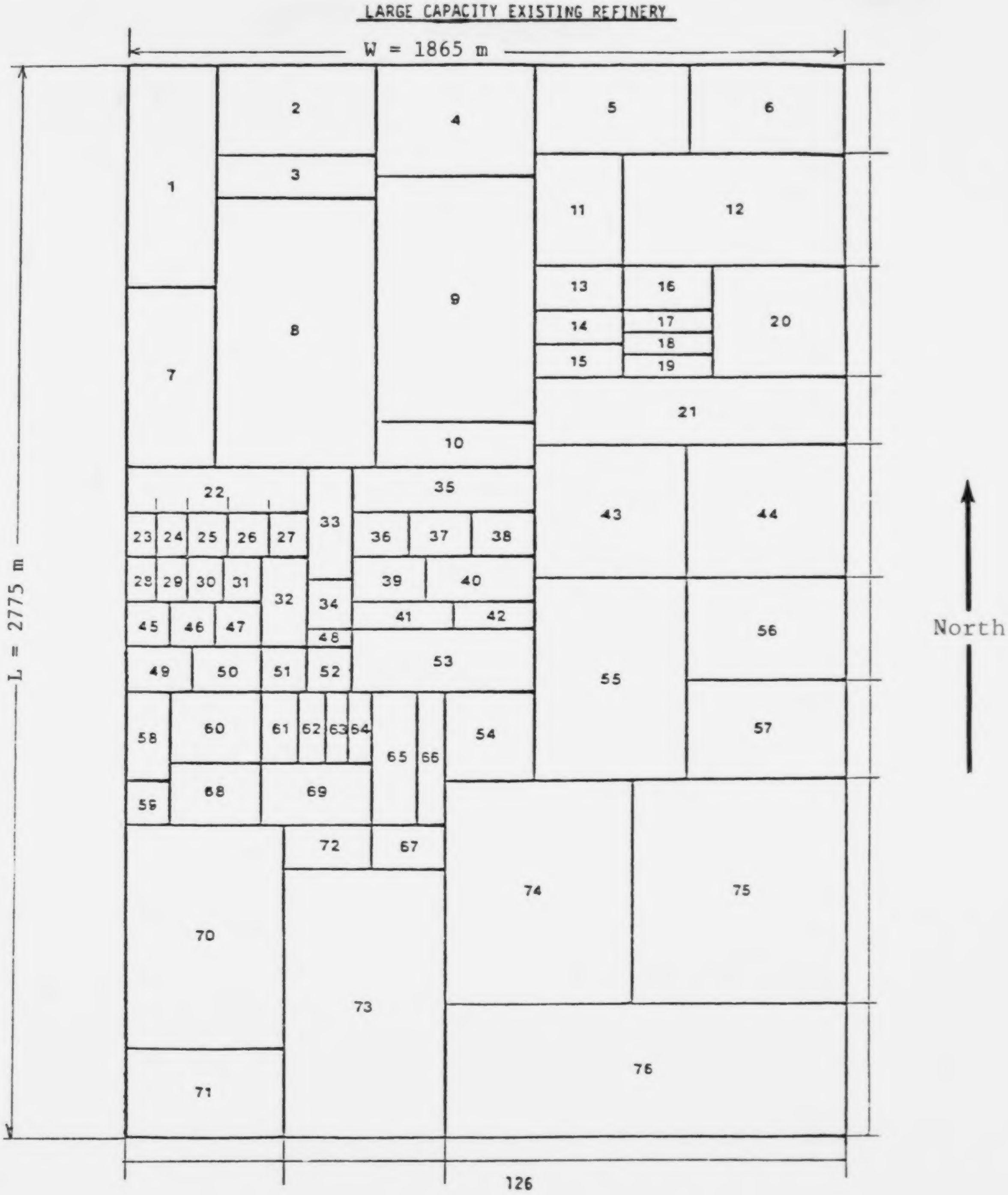
LARGE CAPACITY EXISTING REFINERY
W = 1865 m
L = 2775 m
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Figure D2-2. Model refinery layout[2]

TABLE D2-1. LARGE CAPACITY EXISTING REFINERY MODULE KEY[2]

Module No.	Description	Module No.	Description
L1	Buffer Zone	L36	Catalytic Reformer
L2	Feedstock Storage	L37	Aromatics Extraction
L3	Crude Oil Storage	L38	Catalytic Cracking
L4	Feedstock Storage	L39	Para-Xylene Plant
L5	Feedstock Storage	L40	Delayed Coker
L6	Crude Oil Storage	L41	Barrel Storage
L7	Feedstock and Product Storage	L42	Barrel Reconditioning
		L43	Feedstock Storage
L8	Crude, Feedstock, and Product Storage	L44	Storm Water Impound Basin
L9	Crude, Feedstock, and Product Storage	L45	Warehouse
		L46	Gas Holder/Blowdown Stack
L10	Oil-Water Separator		
L11	Product Storage	L47	Gas Holder/Blowdown Stack
L12	Product Storage		
L13	Distillation and Gas Recovery Unit	L48	Fire Prevention Training Facility
L14	Jet Hydrofiner/Catalytic Reformer	L49	Oil-Water Separator
		L50	Asphalt Plant
		L51	Solvent Treating Plant/ Boiler House
L15	Naphtha Hydrotreater		
L16	Hydrotreater (Lt Cycle Oil)	L52	SO_2 Treating Plant/ Tanks
L17	Hydrogen Manufacturing	L53	Lube Oil Packaging
L18	Partial Oxidation Unit	L54	Coke Storage
L19	Future Expansion	L55	Crude Oil Storage
L20	Cooling Tower	L56	Feedstock Storage
L21	Flares	L57	Tanks/Impound Basin
L22	Feedstock and Product Storage	L58	Administration
		L59	Oil-Water Separator
L23	Naphtha Hydrotreater	L60	Gasoline Sweetener/ Crude Distillation
L24	Vacuum Gas Oil Unit		
L25	Benzene Fractionation	L61	Crude Distillation/ Crude Desalter
L26	Steam Rerun Stills		
L27	Future Expansion	L62	Specialty Crude Distillation
L28	Crude Distillation		
L29	Catalytic Reformer	L63	Speciality Crude Distillation/Condenser Box
L30	Vacuum Residum Desulfurizer		
L31	Hydrogen Manufacturing	L64	Gasoline Fractionating Unit
L32	Alkylation		
L33	Distillate Hydrodesulfurization (Hvy Gas Oil)	L65	Tank Loading/Truck Loading/Vapor Recovery
L34	Sulfur Recovery	L66	Buildings
L35	Tanks/Cooling Towers	L67	LPG Storage and Blending
L68	Vapor Recovery/Gasoline Rectifier/Tanks		
L69	Main Pump House		
L70	Product Storage		
L71	Wastewater Treatment		
L72	Building		
L73	Product Storage		
L74	Shops and Warehouse		
L75	Crude Oil Storage		
L76	Crude, Feedstock, and Product Storage		

The oil/water separator in Module L10 treats aqueous discharge from Modules L1-L21.

The separator located in Module L59 treats aqueous streams from Modules L58-L60, L70, L71, and L73-L76.

The wastewater separator in Module L49 treats discharges from the remaining modules.

3.0 EMISSION CALCULATIONS

Once the model refinery is defined, the next step is to estimate its emissions. For point source emissions, available emission factors are used. For fugitive emissions, both emission factors and fitting counts are required. Finally, the total hydrocarbon emissions are broken down into emissions of selected hydrocarbon components.

3.1 Emission Factors and Fitting Counts

Emission factors and the corresponding unit capacities for the model refinery are presented in Table D3-1. All of these emission factors were taken from AP-42[3] with the exception of the non-methane hydrocarbon factor from the FCC unit CO boiler and the SO_x factors from the Sulfur Recovery Complex.

Table D3-2 presents estimated fitting counts and emission factors for fugitive sources in the model refinery. All of these emission factors were taken from Radian testing except for those for the oil/water separator.

The estimate of the population of each type of fitting is as important as the emission factor in determining total emissions. The PES model contained estimates of fitting populations, but they were not broken down into the service categories corresponding to the emission factors. Radian data on fitting counts were generated during the field testing phase (see Table D3-3), but these unit configurations would not necessarily match those from the model refinery. The following procedure was developed to generate fitting counts compatible with emission factor service classes and to represent the model refinery as closely as possible:

TABLE D3-1. PROCESS SOURCES AND EMISSION FACTORS

SOURCE	CAPACITY	EMISSION FACTORS				
		PARTICULATES	SO_x	NO_x	CO	NM HYDROCARBONS
Process Heaters/Boilers						
- oil fired[1]	36.7 x 10^3 gal/hr	6 lb/10^3 gal	47.7 lb/10^3 gal	60 lb/10^3 gal	5 lb/10^3 gal	1 lb/10^3 gal
- gas -fired[2]	2.27 x 10^6 ft^3/hr	5 lb/10^6 ft^3	0.6 lb/10^6 ft^3	120 lb/10^6 ft^3	17 lb/10^6 ft^3	3 lb/10^6 ft^3
Fluid Catalytic Cracker CO Boiler[3]	2.086 x 10^3Bbl/hr	45 lb/10^3Bbl	493 lb/10^3Bbl	71 lb/10^3Bbl	Negligible	13.3 lb/10^3Bbl
Sulfur Recovery Complex[4]						
- Claus plants plus Wellman-Lord Tail Gas Treating Unit	408 long tons/day (LTPD)	--	3.6 lb/LT	--	--	--
- Sulfuric Acid Plant	179 LTPD	--	14.6 lb/LT	--	--	--
Flares[5]	350 x 10^3Bbl/day	Negligible	26.9 lb/10^3Bbl	18.9 lb/10^3Bbl	4.3 lb/10^3Bbl	0.8 lb/10^3Bbl

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[1] Based on AP-42[3] factors for No. 6 Fuel Oil with 0.3 wt. % sulfur.

[2] Based on AP-42[3] factors for natural gas.

[3] Based on AP-42[3] factors for a Fluid Catalytic Cracker with an Electrostatic Precipitator and a CO Boiler, except the NMHC factor was taken from Radian testing.

[4] Based on sulfur recovery efficiencies taken from Hydrocarbon Processing;[4] 2-stage Claus = 92%, Wellman-Lord TGTU = 99%, Sulfuric Acid Plant = 99%

[5] Based on AP 42[3] factors for blowdown systems with vapor recovery and vents to flares.

TABLE D3-2. FUGITIVE SOURCES AND EMISSION FACTORS

SOURCE	ESTIMATED POPULATION (OR CAPACITY)	SERVICE CATEGORY	NON-METHANE HYDROCARBON (NMHC) EMISSION FACTORS
Pump Seals[1]	313	Light Liquid	0.25 lb/hr./source
	340	Heavy Liquid	0.046
Valves[1]	1714	Hydrogen	0.018
	4198	HC Gas	0.059
	7422	Light Liquid	0.024
	8442	Heavy Liquid	0.0005
Compressor Seals[1]	82	Hydrogen	0.11
	48	HC Gas	1.40
Flanges[1]	84346	NA	0.00056
Relief Valves[1]	171	NA	0.19
Process Drains[1]	1105	NA	0.070
Cooling Towers[1]	(10,668 x 10^3 gal/hr)	NA	0.006 lb/10^3 gal.
Oil/Water Separators[2]	(160.3 x 10^3 gal/hr)	Uncontrolled	5.0 lb/10^3 gal.
	(1719 x 10^3 gal/hr)	Controlled	0.2 lb/10^3 gal.
Dissolved Air Flotation[1]	(220.5 x 10^3 gal/hr)	NA	0.01 lb/10^3 gal.

[1] Emission factors based on Radian testing.
[2] Emission factors based on AP-42.

1) Use PES pump count times 1.4 to estimate the total number of pump seals. Use pump service descriptions to determine the service class, with naphthas and lighter being light liquids, all others being heavy liquids.

2) Use PES compressor count times 2 to estimate the total number of compressor seals. Use compressor service descriptions to determine the percentage in hydrocarbon and/or hydrogen service.

3) Use the pump seal count times 41 to estimate total valves.

4) Use the percentage in gas service from the technical memorandum, and split the total valves in gas service into 29 percent hydrogen and 71 percent hydrocarbon service.

5) Break down valves in liquid service into light liquid and heavy liquid based on the breakdown of pumps for that unit.

6) Use the valve count times 4 to estimate the total number of flanges.

7) Use the process drain count from Table D3-3. If none is available for a given unit, use the pump seal count times 1.9.

TABLE D3-3. ESTIMATED NUMBER OF INDIVIDUAL EMISSION SOURCES IN 15 SPECIFIC REFINERY PROCESS UNITS

Process Unit	Estimated Number of Sources Within Battery Limits of Process Units					
	Valves	Flanges	Pumps[3]	Compressors[4]	Drains	Relief Valves
Atmospheric Distillation	890	3540	31	1	69	6
Vacuum Distillation[1]	500	2700	16	0[1]	35	6
Fuel Gas/Light Ends Processing	180	760	3	2	11	6
Catalytic Hydroprocessing	650	2600	10	3	24	6
Catalytic Cracking	1310	5200	30	3	65	6
Hydrocracking	930	3760	22	3	58	6
Catalytic Reforming	690	2760	14	3	49	6
Aromatics Extraction[1]	600	2400	18[1]	0[1]	41	6
Alkylation	680	2280	11	0	41	6
Delayed Coking[1]	300	1240	9[1]	0[1]	28	6
Fluid Coking	300	1240	9	4	28	6
Hydrodealkylation[1]	690	3760	14[1]	3[1]	58	6
Treating/Dewaxing	600	2290	18	1	44	6
Hydrogen Production	180	640	5	3	17	4
Sulfur Recovery[1]	200	800	6[1]	0[1]	20	4

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[1] Sources were not counted in process units of this type. The number of sources was estimated.
[2] Only those sources in hydrocarbon (or organic compound) service.
[3] Number of pump seals - 1.4 x number of pumps.
[4] Number of compressor seals - 2.0 x number of compressors.

8) Estimate the number of relief valves as an average of 6 per unit. This average was developed from field source counts.

The figures for capacity of various process units and wastewater treating facilities were taken directly from the PES report.

Although emissions from storage tanks were not within the scope of this study, they were estimated to provide a basis of comparison to other hydrocarbon emission sources. The PES report contained a detailed breakdown of the storage facilities, their service, capacities, and annual turnover. Emission factors were taken from AP-42[3] and applied to these facilities to estimate total emissions. The PES data indicated the use of floating roofs to control emissions on all tanks containing liquids with Reid vapor pressures greater than 0.5 psia. This stringent level of control probably explains the low estimate of storage emissions as compared to other hydrocarbon sources in the model refinery (see Table D3-4).

3.2 Emissions of Criteria Pollutants and Total Hydrocarbons

By applying the appropriate emission factors, unit capacities, and fitting counts documented in Section 3.1, a slate of emissions from the model refinery can be estimated. Table D3-4 is a summary of those emissions by pollutant type and by source.

TABLE D3-4. SUMMARY OF EMISSIONS FROM THE MODEL REFINERY

	Emissions in Tons/Year			
Pollutant	Point Sources[1]	Fugitives[2]	Storage	Total
Particulates	1,425	-----	-----	1,425
SO_x	14,650	-----	-----	14,650
CO	1,247	-----	-----	1,247
NO_x	12,693	-----	-----	12,693
Non-Methane Hydrocarbons	364	8,767	3,308	12,439

[1] Includes combustion sources, fluid catalytic cracker, CO boiler, sulfur recovery complex, and flares.

[2] Includes process fittings (pumps, valves, flanges, compressors, drains, and relief valves), cooling towers, oil/water separators, and other wastewater treating units.

3.3 Emissions of Selected Hydrocarbon Components

The emissions estimates in Table D3-4 are sufficient inputs to the model to estimate the ambient concentrations of criteria pollutants, but a species breakdown is necessary to evaluate specific hydrocarbon concentrations. Analyses of the components in various process streams were made in this program and supplemented by literature sources. The application of these stream analyses is not straightforward, however, since the emissions were estimated on a unit basis. The necessary approach involves three steps:

- Distribute total unit emissions among the appropriate streams.
- Apply stream analyses to get component emissions for each stream.
- Sum the stream component emissions to get unit component emissions.

First the unit emissions must be broken down into the streams characteristic of that unit. As an example, Table D3-5 shows the breakdown for the fugitive emissions from the fluid catalytic cracker. It's characteristic streams are:

- Atmospheric gas oil (feedstock).
- FCC Make-gas.
- Olefinic LPG.
- Cracked naphtha.

TABLE D3-5. DISTRIBUTION OF UNIT FUGITIVE EMISSIONS BY STREAM

	Example: Fluid Catalytic Cracking Unit			
Stream	Percent of Fittings for the Stream Ⓐ	Weighted Emission Factor for the Stream Ⓑ lb/hr/source	Relative Emission Rate for the Stream Ⓐ × Ⓑ	Percent of Unit Fugitive Emissions for the Stream
Atmospheric Gas Oil	15	0.0016	0.024	1
FCC Make-gas	10	0.059	0.59	30
Olefinic LPG	15	0.030	0.45	23
Cracked Naphtha	30	0.030	0.9	45
Lt. Cycle Gas Oil	20	0.0016	0.032	1
Hvy. Cycle Gas Oil	10	0.0	0.0	0
Totals	100	N.A.	1.996	100

- Light cycle gas oil.
- Heavy cycle gas oil.

Although this does not include every possible product or intermediate stream, it is detailed enough to allow a reasonably good characterization.

The next step is to estimate the percentage of total fittings in each stream service. These are engineering estimates based on familiarity with the unit operations. The next important variable is the weighted emission factor for each stream. This is determined by first classifying the stream as gas phase, light liquid, heavy liquid, or hydrogen. For gas phase and hydrogen service, the valve emission factor was used as the weighted average indicator. For light and heavy liquids, a ratio of 41 valves per pump was used to estimate the weighted average indicator. Since valves and pumps contribute greater than 70 percent of the process fugitive emissions, it is reasonable to base the weighted average emission factor on them alone. It should also be noted that this factor is being used only to compare the relative emissions contribution of each stream, not as an absolute value to calculate emissions. When these two factors are multiplied together, the resulting product is in proportion to each stream's tendency to cause fugitive emissions. By summing these products and determining each product as a percentage of the sum, the total unit emissions can be allocated to each stream by that percentage.

Next the component analyses can be applied to these stream emissions. The component analyses come primarily from GC-MS work done on samples collected in the refineries during fugitive emission sampling. This was supplemented where necessary with data from a previous Radian literature survey,[3] an API medical research report,[4] and engineering estimates. Tables D3-6 and D3-7 are examples of a GC-MS data sheet and the stream quality summary, respectively. All of the GC-MS data sheets are included in Appendix B, Section 5.

It was necessary to consolidate these component analyses to minimize calculations and to yield reasonable data. This consolidation was done on the basis of the availability of both discrete concentration data and quantifiable toxicity data for any given component. If both were available, then the component was treated individually. If either was missing, the component was lumped into a family of components such as "other alkylbenzenes." This resulted in a list of discrete components which included:

- Benzene.
- Toluene.
- Ethylbenzene.
- Mixed xylenes.
- Naphthalene.
- Anthracene.
- Biphenyl.
- Hexane

TABLE D3-6. EXAMPLE STREAM COMPONENT ANALYSIS-CRACKED NAPHTHA

Peak Number	Compounds (In Retention Order)	Bulk Liquid (ppm)	Vapor on XAD (µg)	Vapor on Tenax (µg)
1	Benzene	6,600	260	0.72
(IS)	d_6-Benzene	--	--	(0.035)
2	Toluene	47,700	8,100	25.3
3	Ethylbenzene	10,600	4,400	4.0
4	m-+p-Xylene	57,200	8,000	21.3
5	o-Xylene	21,300	7,500	8.7
6	Isopropylbenzene	--	130	0.21
7	n-Propylbenzene	3,000	850	19.8
8	3- + 4-Ethyltoluene	32,500	7,100	
9	1,3,5-Trimethylbenzene	15,100	2,800	
10	2-Ethyltoluene	7,100	1,280	
11	1,2,4-Trimethylbenzene	46,000	6,150	13.3
12	1,2,3-Trimethylbenzene	9,600	880	3.2
13	C_4-Alkylbenzene	--	72	0.33
14	Indan	4,000	250	1.2
15	C_4-Alkylbenzene	17,200	1,000	7.8
16	C_4-Alkylbenzene	19,600	960	
17	C_4-Alkylbenzene	2,400	210	
18	C_4-Alkylbenzene	13,200	520	4.1
19	C_4-Alkylbenzene	13,600	480	
20	2- Methylindan	2,500	85	0.41
21	C_4-Alkylbenzene	2,000	32	0.74
22	C_4-Alkylbenzene	19,600	340	2.3
23	Methylindan	2,500	10	0.22
24	Methylindan	2,800	30	0.24
25	C_4-Alkylbenzene	2,800	--	0.49
26	C_5-Alkylbenzene	27,000	--	1.2
27	C_5-Alkylbenzene	2,700	--	0.44
28	Naphthalene	15,600	66	0.03
29	C_4-Alkylbenzene	1,200	--	--
30	C_2-Alkylindan	2,400	--	0.11
31	C_4-Alkylbenzene	600	--	--
32	C_5-Alkylbenzene	4,000	--	1.2
33	C_5-Alkylbenzene	1,700	--	0.46
34	C_2-Alkylindan	400	--	--

Continued

TABLE D3-6. CONTINUED

Peak Number	Compounds (In Retention Order)	Bulk Liquid (ppm)	Vapor on XAD (μg)	Vapor on Tenax (μg)
35	C_2-Alkylindan	600	--	--
36	C_2-Alkylindan	400	--	--
37	C_2-Alkylbenzene	100	--	--
38	C_5-Alkylbenzene	1,000	--	--
39	2-Methylnaphthalene	8,700	--	0.03
40	1-Methylnaphthalene	3,600	--	0.01
(IS)	d_{10}-Anthracene (IS)	(100)	(1,000)	--

TABLE D3-7. SUMMARY OF STREAM QUALITY DATA (PPMW)

Compound or Functional Family	Crude Oil	Straight Run Naphtha	Middle Distillate	Atmospheric Gas Oil	Vacuum Gas Oil	Reformate	H_2 Recycle Gas	Desulfurized Naphtha
Benzene	60	253	0	0	0	5,400	0	253
Toluene	680	2,621	5	8	5	77,700	0	2,621
Ethylbenzene	220	887	9	6	6	33,500	0	887
Xylenes	880	1,623	52	16	22	170,900	0	1,623
Other Alkylbenzenes	3,739	16,578	815	61	368	324,400	0	16,578
Naphthalene	260	1,463	100	4	28	7,400	0	1,463
Anthracene	140	5	56	3	12	0	0	5
Biphenyl	320	628	0	0	9	0	0	628
Other PNA's	7,880	14,983	5,507	220	663	700	0	14,983
n-Hexane	18,000	38,838	0	0	0	24,000	0	38,838
Other Alkanes	877,240	499,613	842,536	949,673	948,887	356,000	650,000	499,613
Olefins	0	0	0	0	0	0	0	0
Cycloalkanes	58,300	422,508	100,000	50,000	50,000	0	0	422,508
Other Compounds Indicated Present	Carbonyl ~ 500 ppm Thiols ~ 25,000 ppm Sulfides ~ 6,000 ppm Quinolines ~ 200 ppm Pyridines	Pyridines Thiols Sulfides	Pyridines Thiols Sulfides ~ 51,000 ppm Quinolines	Pyridines Thiols Sulfides Quinolines ~ 9 ppm	Pyridines Thiols Sulfides Quinolines		H_2 ~ 350,000	

TABLE D3-7. CONTINUED

Compound or Functional Family	Hydrotreated Middle Distillate	Refinery Fuel Gas	Liquefied Petroleum Gas (LPG)	Raffinate	Aromatics Extract	Benzene	Toluene	Xylenes
Benzene	0	0	0	50	17,840	993,000	1,000	0
Toluene	5	0	0	750	256,700	2,000	992,800	1,000
Ethylbenzene	9	0	0	300	110,670	0	4,000	162,420
Xylenes	52	0	0	1,500	564,590	0	1,000	828,580
Other Alkylbenzenes	835	0	0	2,300	48,000	0	0	5,000
Naphthalene	100	0	0	50	100	0	0	100
Anthracene	56	0	0	0	0	0	0	0
Biphenyl	0	0	0	0	0	0	0	0
Other PNA's	5,507	0	0	50	100	0	0	100
n-Hexane	0	0	0	63,000	100	5,000	0	0
Other Alkanes	887,436	920,000	1,000,000	932,000	1,900	0	1,200	2,800
Olefins	0	60,000	0	0	0	0	0	0
Cycloalkanes	100,000	0	0	0	0	0	0	0
Other Compounds Indicated Present	Sulfides ≅ 6,000 ppm	H_2 ≅ 20,000 Thiols Sulfides	Thiols Sulfides					

TABLE D3-7. CONTINUED

Compound or Functional Family	LPG Olefins	Alkylate	Cracked Naphtha	FCC Light Cycle Gas Oil	FCC Heavy Cycle Gas Oil	Heavy Aromatics Extract (SO_2 Plant)	Asphalt	API Separator Skim Oil	Vacuum Resid
Benzene	0	0.1	2,880	0	740	0	0	87	0
Toluene	0	0.3	89,780	40	10,000	0	0	1,713	0
Ethylbenzene	0	0.1	21,430	0	1,200	0	0	661	0
Xylenes	0	1.1	171,450	610	11,800	0	0	2,510	0
Other Alkylbenzenes	0	3.3	243,470	26,670	38,200	750,000	*i*	12,751	*i*
Naphthalene	0	0.3	10,950	59,000	14,000	0	0	990	0
Anthracene	0	0	0	10,270	0	0	2	457	2
Biphenyl	0	0	0	10,180	0	0	0	2,351	0
Other PNA's	0	2.2	6,480	624,480	22,500	200,000	200	29,700	200
n-Hexane	0	96	11,830	0	0	0	0	*i*	0
Other Alkanes	400,000	998,956	204,110	190,800	701,560	45,000	999.798	948,780	999,798
Olefins	600,000	930	170,740	36,750	50,000	0	*i*	*i*	
Cycloalkanes	0	11	68,880	41,200	150,000	5,000	*i*	*i*	
Other Compounds Indicated Present	Thiols		Pyridines Thiols Sulfides Quinolines	Phenols Carbonyls Pyridines Thiols Sulfides Quinolines	Pyridines Carbonyls Thiols Sulfides Quinolines				

Note: The symbol *i* means that the component has been indicated to be present, but the exact concentration is unknown.

The general family groups included:

- Other alkylbenzenes.
- Other polynuclear aromatics.
- Other alkanes.
- Olefins.
- Cycloalkanes.

It is not really meaningful to talk about the toxicity of such a broad group as olefins or cycloalkanes. These were included to assure a consistent analysis based on a closed mass balance to be synthesized from several diverse sources.

The dispersion model inputs emissions on a unit basis, so the next step is to combine the stream breakdown with the stream analyses to get a component analysis of unit emissions. An example of this process is shown for fugitive emissions from the FCC in Table D3-8.

A similar operation was performed separately on relief valves, since they are not distributed uniformly across the streams. Relief valves are usually placed at the top of a fractionating column or reactor vessel, and thus are exposed primarily to lighter streams. Table D3-9 shows the allocation of relief valves for the Aromatics Fractionation Unit. The number of relief valves in each stream service was then totaled, and the stream analyses were applied to the emissions, as shown in Table D3-10. According to observations in the refineries tested, few relief valves in existing refineries are vented to a control

TABLE D3-8. FLUID CATALYTIC CRACKING - FUGITIVE EMISSION CHARACTERIZATION

		Weighted Contribution of each Component to Unit Emissions, in ppmw													
Stream	% of Unit Fugitives Attributable to that Stream	Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Polynuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
Atmos. Gas Oil	1	0	0	0	0	1	0	0	0	2	0	9495	0	500	0
Fuel Gas	30	0	0	0	0	0	0	0	0	0	0	276000	18000	0	6000
LPC Olefins	23	0	0	0	0	0	0	0	0	0	0	92000	138000	0	0
Cracked Naphtha	45	1296	40401	9644	77153	109562	4928			2916	5324	91850	76833	30096	0
Lt. Cycle Gas Oil	1	0	0	0	6	267	590	103	102	6245	0	1906	368	412	0
Hvy. Cycle Gas Oil	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total		1296	40401	9644	77159	109830	5518	103	102	9163	5324	471251	233201	31008	6000
Emiss. Rate lb/hr	59.8	.078	2.42	.577	4.61	6.57	.33	.006	.006	.548	.318	28.18	13.95	1.85	.359

TABLE D3-9. RELIEF VALVE DISTRIBUTION

Example: Aromatics Fractionation Unit

Total Relief Valves = 6

Stream	No. of Relief Valves
Benzene	4
Toluene	2
Xylenes	0

TABLE D3-10. RELIEF VALVE SUMMARY FUGITIVE EMISSION CHARACTERIZATION

Total # Relief Valves in that Service	Stream	% of RV Fugitives Attributable to that Stream	Weighted Contribution of each Component to RV Emissions, in ppmv													
			Benzene	Toluene	Ethylbenzene	Xylenes	Other Alkylbenzenes	Naphthalene	Anthracene	Biphenyl	Other Polynuclear Aromatics	n-Hexane	Other Alkanes	Olefins	Cycloalkanes	H_2
(42)	H_2 Recycle Gas	22.5	0	0	0	0	0	0	0	0	0	0	146250	0	0	78750
(12)	Fuel Gas	6.5	0	0	0	0	0	0	0	0	0	0	59800	3900	0	1300
(58)	LPG	31.1	0	0	0	0	0	0	0	0	0	0	311000	0	0	0
(4)	LPG Olefins	2.2	0	0	0	0	0	0	0	0	0	0	8800	13200	0	0
(33)	S.R. Naphtha	17.6	45	461	156	286	2918	257	1	111	2637	6835	87932	0	74361	0
(13)	Cracked Naphtha	7.0	202	6285	1500	12002	17043	767	0	0	454	828	14288	11952	4682	0
(8)	Reformate	4.3	232	3341	1441	7349	13949	318	0	0	30	1032	15308	0	0	0
(2)	Extract	1.1	196	2824	1217	6210	528	1	0	0	1	1	21	0	0	0
(2)	Raffinate	1.1	1	8	3	17	25	1	0	0	1	693	10252	0	0	0
(4)	Benzene	2.2	21846	44	0	0	0	0	0	0	0	110	0	0	0	0
(2)	Toluene	1.1	11	10921	44	11	0	0	0	0	0	0	13	0	0	0
(4)	SO_2	2.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
(2)	Middle Distillate	1.1	0	0	0	1	9	1	0	0	61	0	9828	0	1100	0
	TOTALS	100.0	22533	23884	4361	25876	34472	1345	1	111	3184	9499	663492	29052	80143	80050
	Normalized Total		23040	24421	4459	26458	35247	1345	1	113	3256	9713	678416	29705	81946	81850

device. All relief valves in the model refinery are assumed to vent to the atmosphere.

Still a different procedure was required to characterize the hydrocarbons emitted from the API separators. Analyses were available of the inlet oil to the separator and the recovered oil. A hydrocarbon material balance was then made to determine the composition of the evaporative emissions from the separator, as shown in Table D3-11. The available analyses showed only the aromatic components, so the balance of the oil was assumed to fall in the alkane family.

This material balance approach assumes that any component lost from the oil phase is lost as evaporative emissions. This neglects the slight solubility of certain components which could result in mass transfer to the water phase (or eventually even the sludge phase). This results in another conservatively high, worst case assumption.

3.4 Summary of Hydrocarbon Species Emissions

The emissions of selected hydrocarbon species were calculated by the above methods. The results are summarized in Table D3-12. These figures represent only fugitive hydrocarbon emissions and not the point source emissions from process heaters, fluid catalytic cracking regeneration, etc. The stack hydrocarbon emissions did not significantly affect any of the critical points for hydrocarbon species because of the effects of height of release and plume rise.

TABLE D3-11. ESTIMATED COMPOSITION OF INLET OIL, HYDROCARBON VAPOR, AND OUTLET OIL STREAMS AROUND AN API SEPARATOR

	Estimated Composition of Streams Wt %		
Component	Inlet Oil	Vapor From Separator	Outlet (Skimmed) Oil
Benzene	0.03	0.07	0.01
Toluene	0.22	0.22	0.22
Ethylbenzene	0.06	0.06	0.06
Xylenes	0.21	0.21	0.21
Alkylbenzenes	0.80	0.80	0.80
Naphthalene	0.29	0.29	0.29
Anthracene	0.04	0.04	0.04
Biphenyl	0.18	0.18	0.18
Polynuclear Aromatics (PNA's)	2.04	0.15	2.98
Alkanes	96.13	97.98	95.21
	100.00	100.00	100.00

Skimmed Oil Rate = 667 lb./1000 lb. inlet oil

Vapor Lost from Separator = 333 lb./1000 lb. inlet oil

TABLE D3-12. SUMMARY OF HYDROCARBON SPECIES EMISSIONS FROM FUGITIVE SOURCES

Component	Source							
	V, P, C, F, D, CT*		Relief Valves		API Separators		Totals	
	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr	ppmw	kg/hr
Benzene	7,200	2.8	23,000	0.4	700	0.4	3,900	3.6
Toluene	21,000	8.2	24,000	0.4	2,200	1.1	11,000	9.7
Ethylbenzene	5,600	2.2	4,500	0.1	590	0.3	2,800	2.6
Xylenes	31,000	12.1	26,000	0.4	2,100	1.1	15,000	13.6
Other Alkylbenzenes	42,000	16.6	35,000	0.6	7,900	4.1	23,000	21.3
Naphthalene	1,700	0.7	1,400	0.02	2,900	1.5	2,400	2.2
Anthracene	20	0.01	1	0.0	390	0.2	220	0.2
Biphenyl	230	0.1	110	0.0	1,800	0.9	1,100	1.0
Other PNA's	7,700	3.0	3,300	0.05	1,500	0.8	4,200	3.9
n-Hexane	16,000	6.3	9,700	0.2	*i***	*i*	7,100	6.5
Other Alkanes	654,000	255.9	678,000	11.3	980,000	502.4	840,000	769.6
Olefins	46,000	18.1	30,000	0.5	*i*	*i*	20,000	18.6
Cycloalkanes	135,000	52.9	82,000	1.4	*i*	*i*	59,000	54.3
Hydrogen	31,000	12.3	82,000	1.4	*i*	*i*	15,000	13.7
TOTALS		391.2		16.8		512.8		920.8

*Fugitive emissions from valves, pumps, compressors, flanges, drains, and cooling towers.

**Components marked with "*i*" are indicated present, but no quantifiable concentration data were available.

4.0 ATMOSPHERIC DISPERSION MODELING

With the hypothetical refinery and its emissions defined, the next step is to predict ground level concentrations of the various pollutants. This can be done by using any one of a large variety of computer modeling techniques. This section will discuss the rationale behind the choice of the model used and will give the details of its application to the hypothetical refinery.

4.1 Choice of the Dispersion Model

There are a variety of atmospheric dispersion models available, each with distinct advantages in certain situations. Many of the more sophisticated models have been developed to account for unusual conditions of site topography, meteorological conditions, etc. These models would add little to this analysis of a hypothetical refinery because no hard data for such variables are available.

There are several guidelines to be used in choosing a model. First it should be an established, well accepted model. It should have the capacity to handle a large number of both point sources and area sources. It must be able to give not only the total concentration of the pollutant at any given point, but also the relative contribution of each source to that total.

Although not alone in satisfying these requirements, the EPA guideline model RAM is certainly the most well-known. There are two versions of RAM, the rural and urban verions. The urban version has slightly higher dispersion coefficients to account for the numerous heat sources typical of an urban environment. As with other unconstrained choices, the worst case was chosen, which means the rural version of RAM. The rationale behind always choosing worst case conditions is the desire to generalize the results of the hypothetical refinery analysis. If the worst case analysis shows little or no impact, then it can be said with some confidence that refineries in general have little or no impact. The worst case scenario is softened somewhat by the omission of storage tank emissions from the modeling, but the effects of this will be discussed in the conclusions section.

The choice between the urban and rural versions of RAM is not straightforward. A case could be made for the use of the urban model with larger dispersion coefficients because of the "heat island" effect of the refinery itself. While this approach might better simulate the "real world" effects of the refinery, it would make it impossible to draw any conclusions from the results of the environmental assessment. It should also be noted that the primary objective of this assessment is not the prediction of absolute values of various pollutant concentrations outside the hypothetical refinery, for that would not be possible given the general nature of the refinery model and the state-of-the-art for both emissions estimating and atmospheric modeling. The results of this assessment are intended to show the relative impacts of the many sources in a refinery and to draw rough conclusions as to the potential health effects of refinery emissions. With these objectives in mind, the use of the RAM rural model was justified.

4.2 Application of the Dispersion Model to the Hypothetical Refinery

The air quality impacts of the model refinery were predicted with RAM, an EPA guideline model.[8] It is capable of predicting a 1- to 24-hour average concentration of relatively unreactive pollutants. A maximum of 250 point and 100 area sources can be modeled. Concentrations are predicted at a maximum of 150 selected locations (receptors).

RAM uses Gaussian steady-state dispersion algorithms for areas where one wind vector for each hour is a good approximation. Concentrations are calculated hour by hour as if the atmosphere had achieved a steady-state condition.

One set of inputs to the model are hourly meteorological data consisting of:

Variable	Assigned Value
• Wind speed	4.5 m/sec
• Wind direction	Worst case - Due West
• Temperature	25°C
• Stability class	C
• Mixing height	500 m

These meteorological parameters are set by the "standard receiving atmosphere" as defined by Monsanto in their source severity work.[1] It is recognized that a persistence of these conditions for a 24-hour period is quite improbable, and that this again results in a worst case approximation of "real world" conditions. The source severity methodology is specific in requiring that these conditions be used, and no provisions were given to incorporate variations when modeling for longer averaging times.

The dispersion coefficients (the Gaussian σ's in the vertical and horizontal directions) are empirically determined as functions of atmospheric turbulence, distance from the source and the concentration averaging time. Thus, the spread of the plume is dependent on these three factors. The atmospheric turbulence is defined by stability classes. These classes, which range from very unstable to neutral to very stable atmospheres, are determined by wind speed and insolation during the day, or wind speed and cloud cover during the night. This relationship is presented in Table D4-1.[9] The most unstable class is A with F the most stable. The C stability class used here is considered neutral.

TABLE D4-1. RELATIONSHIP BETWEEN STABILITY CATEGORIES AND SURFACE METEOROLOGICAL CONDITIONS[9]

Surface Wind Speed (at 10 m), m/sec	Day			Night	
	Incoming Solar Radiation			Thinly Overcast or $\geq 4/8$ Low Cloud	$\leq 3/8$ Cloud
	Strong	Moderate	Slight		
< 2	A	A - B	C		
2 - 3	A - B	B	C	E	F
3 - 5	B	B - C	C	D	E
5 - 6	C	C - D	D	D	D
> 6	C	C	C	D	D

The mixing height was set at 500 meters. This mixing height allows the plumes to rise to their maximum height without causing them to be trapped above or reflected off the upper boundary of the mixing zone.

The worst-case wind direction is dependent on source geometry and emission parameters. The worst-case direction was determined by modeling with the wind coming from 16 directions for one hour each and comparing the predicted concentrations. All the meteorological conditions, except wind direction, are constant for the 24 hours. The alternating wind directions are repeated in sequence every 3 hours (5 degrees either side of and including the worst-case wind direction). Thus, the predicted 24-hour concentration would be the same as the 8-hour and 3-hour concentrations.

Annual concentrations (for comparison with NO_2 NAAQS) can be predicted with Larsen statistics.[10] Using empirically determined ratios, the maximum annual concentration can be determined from mean concentrations for shorter averaging times. These ratios are functions of the standard geometric deviation of the shorter averaging times. Using data collected in 1977 by the Texas Air Control Board, a typical standard geometric deviation of 1.85 per 24-hour NO_x concentration was determined. This figure was determined by averaging the standard geometric deviations reported for about 50 noncontinuous NO_2 monitors located in TACB Region VII (which is located on the upper Texas Gulf Coast). Based on a standard geometric deviation of 1.85, Larsen's model estimates that the ratio of the average 24-hour NO_x concentration to the expected maximum annual concentration would be 4.85.

RAM can accept both point sources and area source inputs. The data required to characterize a point source includes:

- Source coordinate.
- Emission rate.

- Physical height.
- Stack diameter.
- Stack gas exit velocity.
- Stack gas temperature.

Area source parameters consist of the:

- Coordinates of the southwest corner.
- Side length.
- Total area emission rate.
- Effective height.

Stacks, flares, etc., were modeled as point sources. Fugitive emissions were modeled by three different methods.

- As a single point source originating in the center of the process unit plot.
- As a pseudo-area source (where the single point source was divided into three point sources distributed across the unit in a plane perpendicular to the worst-case wind direction).
- As area sources.

It was hoped that the point source approximation would not significantly affect the results, since this type of calculation requires much less computer time. This approach gave very unrealistic boundary line conditions, however, with quite large concentration peaks directly downwind of the unit centerlines and very low concentrations elsewhere. The pseudo-area approach had some smoothing effect, but only the rigorous area source approach gave satisfactory results.

Concentrations from the point sources are a function of the distance downwind and crosswind from the source to the receptor. Concentrations due to area sources are calculated using the narrow plume approximation. This neglects diffusion in the crosswind direction and assumes that an area source consists of many narrow plumed point sources. As a result, any receptor that has no area sources directly upwind receives no contribution to its predicted concentration from area sources. A more detailed discussion of the narrow plume approximation is beyond the scope of this assessment, but the theory and validation of this approach are discussed at length in the references.[11,12,13] The five degree variation in wind persistence did add some dispersion outside the worst-case wind direction streamline.

The locations of a series of permanent receptor sites were also input to the model. The locations consisted of a grid placed in the area of greatest impact as predicted by the worst-case wind direction. The model then calculated the 24-hour average concentration at each receptor. From these data, maximum concentrations were determined. Also, isopleths (lines of equal concentration) were plotted. Not only were the total ambient concentrations displayed for each receptor, but these concentrations were broken up into their component contributions from each of the sources.

5.0 IMPACTS ON AMBIENT AIR QUALITY

The outputs from the atmospheric dispersion model consist of estimated maximum ground level concentrations for criteria pollutants and nonmethane hydrocarbons. In this section, these outputs will be presented and compared to National Ambient Air Quality Standards (NAAQS). In addition, the total hydrocarbon concentrations will be broken down into selected components for comparison to toxicity data. The sensitivity of these results will then be examined and their significance discussed.

5.1 Criteria Pollutants and Total Hydrocarbons

The modeling results for criteria pollutants and nonmethane hydrocarbons are summarized in Table D5-1. Note that the four criteria pollutants do not exceed the NAAQS, those being particulates, oxides of sulfur, oxides of nitrogen, and carbon monoxide. The estimated maximum concentration for nonmethane hydrocarbons does exceed the listed standard, but it should be noted that this is only a guideline standard based on the potential contribution of nonmethane hydrocarbons to oxidants.

The maximum ground level concentration of particulates was 68 $\mu g/m^3$ as compared to the NAAQS of 260 $\mu g/m^3$. It should be noted that this considers only process particulates which result primarily from the FCC and oil fired heaters, and does not include fugitive dust from unpaved roads, construction activities, or coke handling. The point of maximum concentration occurred due west of the refinery center at a distance of 1.5 kilometers from the fence line.

The maximum concentration of SO_x was found to be 288 $\mu g/m^3$ as compared to the NAAQS of 365 $\mu g/m^3$. The maximum

TABLE D5-1. SOURCE SEVERITY FACTORS FOR CRITERIA POLLUTANTS

Pollutant	$\bar{X}_{max}$† µg/m³	F†† µg/m³	S†††
Particulates	68	260	0.26
SO_x	288	365	0.78
CO	16	10,000	0.0016
NO_2	55	100	0.55
Nonmethane Hydrocarbons*	9644	160	60.3

† $\bar{X}_{max}$ is the maximum ground level concentration.

†† F is the acceptable pollutant concentration (which is the NAAQS for criteria pollutants).

††† S is the source severity, with the following decision levels.

if $S \geq 1$: Additional Emission Reduction Probably Required

if $0.1^{**} \leq S < 1.0$: May or May Not Require Additional Emission Reduction

if $S \leq 0.1^{**}$: Additional Emission Reduction Probably Not Required point was due west of the fluid catalytic cracking unit and occurred at one-half kilometer from the refinery boundary.

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* The nonmethane hydrocarbon standard is a guideline standard based on the estimated contribution of hydrocarbons to oxidant formation.

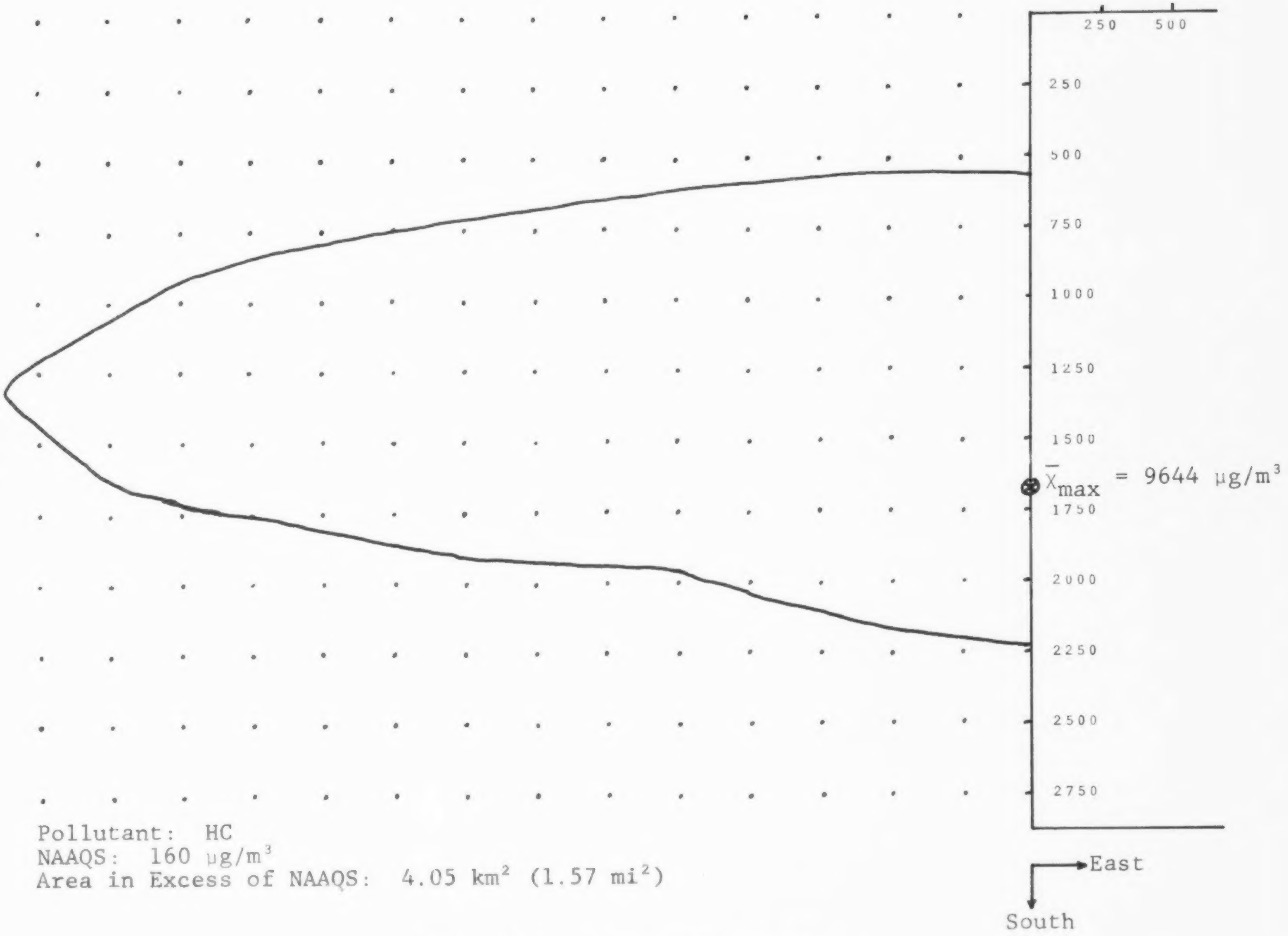
** The lower critical value may need to be as low as 0.01 where large uncertainties are involved.

The maximum 8-hour concentration of CO was predicted to be 17 $\mu g/m^3$ as compared to an NAAQS of 10,000 $\mu g/m^3$. The maximum point occurred due west of the refinery center and at a distance of 1.25 kilometers from the boundary line

The maximum 24-hour average NO_x concentration was estimated to be 269 $\mu g/m^3$. By applying the Larsen statistics discussed in Section 4, the annual average concentration of NO_x was estimated to be 55 $\mu g/m^3$. This figure is well below the NAAQS value of 100 $\mu g/m^3$ as a maximum annual average. Since this analysis used the conservative assumption that all NO_x was emitted as NO_2, the actual NO_2 levels should be even lower.

An analysis of the source severity factors indicates that none of the criteria pollutants has a high probability of causing a public hazard (as indicated by $S \geqslant 1$). On the other hand, only CO has a source severity factor low enough to have strong confidence that it does not create a hazard. The others are in the area of uncertainty where no clear decision can be made, but the worst case scenario used would make the probability of any hazard resulting very low.

The total nonmethane hydrocarbons were found to be in excess of the 160 $\mu g/m^3$ guideline standard, with a maximum concentration of 9644 $\mu g/m^3$. This point was located on the refinery boundary and due west of the main processing area. Although the concentrations fell off rapidly from the maximum, the 160 $\mu g/m^3$ isopleth extends about 3.5 kilometers downwind and encompasses about four square kilometers, as shown in Figure D5-1. The source severity factor for total hydrocarbons is quite high, but



Pollutant: HC
NAAQS: 160 μg/m³
Area in Excess of NAAQS: 4.05 km² (1.57 mi²)

Figure D5-1. Hydrocarbon isopleth

this must be interpreted carefully. The NAAQS guideline for hydrocarbons is based on the prevention of the formation of photochemical oxidants rather than on primary toxicity data. While the health effects and aesthetics of smog are important, more emphasis will be placed on the source severity factors for hydrocarbon components for which toxicity data is available.

5.2 Selected Hydrocarbon Components

The ambient concentration of any given hydrocarbon species can be determined by the following relationship:

$$\bar{X}_s = (\bar{X}_T)\ (PPMW_s)\ (10^{-6})$$

where

$\bar{X}_s$ = the hydrocarbon species ambient concentration contributed by a given source,

$\bar{X}_T$ = the total hydrocarbon ambient concentration contributed by a given source, and

$PPMW_s$ = the concentration in weight parts per million of the subject species in that source.

This is based on the dispersion model assumption that all species will disperse at the same rate; or in other words, that atmospheric turbulence far outweighs any differences in molecular diffusion between species.

The first point of interest is the receptor showing the largest total hydrocarbon concentration. Table D5-2 shows the component breakdown at that point. This maximum point is

TABLE D5-2. HYDROCARBON SPECIES AMBIENT CONCENTRATION AT THE POINT OF MAXIMUM TOTAL HYDROCARBON CONCENTRATION

Location: On the west boundary line at a point 1650 meters from the northwest corner; directly downwind of source L49 (an API separator).

Component	Concentration, $\mu g/m^3$	Concentration, ppmv
Benzene	6.6	0.0019
Toluene	21.2	0.0051
Ethylbenzene	5.7	0.0012
Xylenes	19.8	0.004
Other Alkylbenzenes	102.2	0.017
Naphthalene	27.5	0.0047
Anthracene	3.6	0.0005
Biphenyl	16.5	0.0025
Other Polynuclear Aromatics	22.7	0.0030
n-Hexane	2.8	0.0007
Other Alkanes	9380.0	1.876
Olefins	0.0	0.0
Cycloalkanes	33.7	0.009
H_2	1.8	0.020
Total Nonmethane Hydrocarbons	9644.0 $\mu g/m^3$	1.95 ppmv

located directly downwind of the API separator (Source L-49), and 97.8 percent of the hydrocarbon species at that point came from the separator. The bulk of the hydrocarbons are from the alkane family (9380 μg/m^3 or 1.9 PPMV), but both the aromatics and polynuclear aromatics species are present at the part per billion level (PPB).

It is also desirable to find the point of maximum concentration for each potentially hazardous component, if that should prove to be different from the point of maximum total hydrocarbons. A limited search was carried out to find these species maximum points by finding the maximum points for units with high concentrations of the subject species. For example in the case of benzene, the maximum point for each catalytic reformer, the aromatics extraction unit, the aromatics fractionation unit, and the fluid catalytic cracking unit were determined. A complete component breakdown was calculated at each point to detect unit interactions, and the point of maximum benzene concentration was selected. A similar procedure was carried out for each component, and the resulting maximum concentrations are summarized in Table D5-3.

It is interesting to note that all of the species maximum concentrations came from the two highest ranked points for total hydrocarbons. Five species (including benzene, naphthalene, anthracene, biphenyl, and the general polynuclear aromatics family) have their maximums adjacent to the API separator. The other species maximum values were found at a receptor on the west boundary about 1380 meters from the northeast corner. The largest contributor to this point was the crude distillation unit (L28-1). Other significant contributing units included:

TABLE D5-3. MAXIMUM AMBIENT CONCENTRATION OF SELECTED HYDROCARBON SPECIES

Component	Ambient Concentration		Location
	$\mu g/m^3$	ppmv	On the West Boundary, XXXX meters from the Northeast Corner
Benzene	6.6	0.0019	1650
Toluene	26.3	0.0063	1380
Ethylbenzene	10.7	0.0022	1380
Xylenes	53.6	0.0092	1380
Other Alkylbenzenes	105.5	0.0179	1380
Naphthalene	27.5	0.0047	1650
Anthracene	3.6	0.0005	1650
Biphenyl	16.5	0.0025	1650
Other Polynuclear Aromatics	22.7	0.0030	1650
n-Hexane	58.5	0.0152	1380
Olefins	37.6	0.010	1380
Cycloalkanes	365.8	0.099	1380

- Two catalytic reformers (L36-1 and L29-1).
- Aromatics extraction (L37-1).
- Alkylation (L32-1).
- Fluid catalytic cracker (L38-1).
- Delayed coker (L40-1).
- Hydrogen plant (L31-1).
- Resid HDS (L30-1).

The largest concentration for any single component examined was found to be hexane at a concentration of 15 PPBV.

To assess the impact of a given concentration of a pollutant species, quantifiable toxicity data must be available. The Monsanto approach uses the term "acceptable pollutant concentration" as the level at which there is a very low probability of adverse impacts on the general public. For criteria pollutants, the Primary Ambient Air Quality Standards were used as the acceptable pollutant concentrations. For other species, the acceptable concentration can be estimated from the Threshold Limit Value (TLV) as shown below:

$$F = TLV(G),$$

where

$$G = (8/24)\ (1/100) = 1/300,$$

so

$F = TLV/300.$

The factor "G" is defined as a conversion factor to change a TLV into an "equivalent PAAQS" and is calculated from two factors:

- The ratio (8/24) converts the TLV from an 8-hour per day basis to a 24-hour basis.

- The factor (1/100) is a safety factor to account for the fact that the general public is more susceptible to illness than the industrial work force (for whom the TLV was set).

Table D5-4 shows a summary of the acceptable pollutant concentrations that result from this operation. Note that some of the values are in parentheses. These are values arbitrarily assigned to a family of chemicals, some of whose members have TLV's that average out to the assigned value. These values are interesting, but they should be used with caution. Not all of the members of such a family are equally toxic, nor is it certain that their effects would be additive. If the source severity factors based on these values are low, then it can be said with some confidence that no damage will be done by those compounds. If the values are high, however, no conclusion can be drawn.

The whole process of basing an acceptable pollutant concentration on TLV's should be critically appraised. These values were set for use in industrial hygiene studies within plant boundaries, and the American Conference of Governmental Industrial Hygienists (ACGIH) specifically warns against their use:

TABLE D5-4. SUMMARY OF "F" VALUES

Pollutant	F $\mu g/m^3$	Based on
Benzene	114	TLV = 10 PPM
Toluene	1,388	TLV = 100 PPM
Ethylbenzene	1,586	TLV = 100 PPM
Xylenes	1,586	TLV = 100 PPM
Other Alkylbenzenes	(488)	TLV = (25 PPM)
Naphthalene	194	TLV = 10 PPM
Anthracene	0.66	TLV = 200 $\mu g/m^3$*
Biphenyl	4.4	TLV = 0.2 PPM
Other Polynuclear Aromatics	(25)	TLV = (1 PPM)
n-Hexane	1,281	TLV = 100 PPM
Other Alkanes	(16,665)	TLV = (1,000 PPM)
Olefins	(12,344)	TLV = (1,000 PPM)
Cyloalkanes	(4,937)	TLV = (400 PPM)

*Based on "Coal Tar Pitch Volatiles" of which anthracene is a major component.

- as a relative index of hazard or toxicity,
- in the evaluation of community air pollution, or
- in estimating the toxic potential of continuous, uninterrupted exposure.

While such usage is discouraged, the fact remains that no other source of quantifiable toxicity levels is available. Therefore, the use of TLV's to estimate acceptable pollutant concentrations is used here in accordance with the source severity methodology. It is felt that this comparison, however tenuous it might be, is better than ignoring the problem. This is especially true as long as the proper qualifications and limitations on the results are explicitly stated.

Taking the maximum ambient concentrations presented in Table D5-3 and the acceptable pollutant concentrations shown in Table D5-4, it is straightforward to calculate source severity factors for each component. These factors are shown in Table D5-5.

Using Monsanto's recommended decision levels, it can be said that there is a significant probability that anthracene and biphenyl need further application of control technology. Several things should be noted in that context:

- The high concentrations of these species were contributed by a covered API separator.
- That separator was located right on the plant boundary line, which is quite unusual.

TABLE D5-5. SOURCE SEVERITY FACTORS FOR SELECTED HYDROCARBON SPECIES

Component	$\bar{X}_{max}$ µg/m³	F µg/m³	S
Benzene	6.6	114	0.06
Toluene	26.3	1388	0.02
Ethylbenzene	10.7	1586	0.007
Xylenes	53.6	1586	0.03
Other Alkylbenzenes	105.5	(488)*	(0.22)
Naphthalene	27.5	194	0.14
Anthracene	3.6	(0.66)	(5.5)
Biphenyl	16.5	4.4	3.8
Other Polynuclear Aromatics	22.7	(25)	(0.9)
n-Hexane	58.5	1281	0.05
Olefins	37.6	(12344)	(0.003)
Cycloalkanes	365.8	(4937)	(0.07)

*Values in parentheses are an average of the F values for several selected members of the family group, and are not true F values for the entire family.

- There is a great deal of uncertainty in the emission factor for separators. No conclusive results were obtained from limited testing of separators on this program, so AP-42 factors were used in this analysis. The EPA has since begun a program to improve these factors.

- The emissions from an API separator are highly variable in component breakdown (much more so than process unit emissions), and the species breakdown for that unit is based on several grab samples which may well not be reflective of "typical" operation.

- These component emissions (calculated by an oil-phase volatile hydrocarbon balance) may be overstated due to solubility effects.

It can also be stated that there is a very low probability of the need for further control of ethylbenzene and the olefin family. All other species fall into the range where no clear decision can be made. The uncertainties involved in the calculation of these source severity factors make it impossible to make clean cut decisions for the range from 0.01 to 0.99.

It should also be noted here that all of the quoted hydrocarbon species maximum points occurred on the refinery boundary. Because they are released close to the ground and with little velocity or thermal buoyancy, the vapors tend to stay at ground level. Dispersion does proceed at a relatively rapid pace when moving downwind. This establishes two interesting points:

- The sphere of influence for hydrocarbon species that were noted as potential problems at the boundary line does not extend more than a few hundred meters.

- This further suggests that buffering areas with a high potential for fugitive emissions could be effective in reducing or eliminating high source severities.

5.3 Discussion of Results

The detailed results of the environmental impacts of emissions from the hypothetical refinery were presented in the last section. This section will examine the significance of those results and draw conclusions where possible.

The first step is an examination of all the input variables to see how sensitive the results are to changes in the assumptions that were used. The most significant variables to consider are:

- Refinery processing configuration.

- Refinery layout.

- Calculated emissions.

- Atmospheric dispersion model choice.

- Meteorological conditions.

- Hydrocarbon component breakdown.

- Basic toxicity data.

- Modified toxicity data.

Several of these can be considered in a group. A change in the calculated emission rates will produce a proportional change in the predicted maximum concentrations. These emissions will vary with a change in refinery processing configuration, emission factors, or fitting counts. This in itself is enough to prevent a complete generalization of these results to the refining industry. A simple topping refinery, for instance, will have lower emissions and quite different component breakdowns, probably resulting in lower source severity factors.

Another point of uncertainty is the potential contribution of storage emissions to the impacts predicted for the refinery process area. As described in Section 3, total storage tank emissions were estimated to be 3308 tons per year or about 27 percent of all nonmethane hydrocarbon emissions. These emissions were estimated for each of the storage modules listed in Table D2-1. Since no layout information within the module was available, each storage module was treated as an area source. The specific emission rates ($lb/hr/ft^2$) were calculated for each module and compared to the API separator and the process area which contributed to the two highest points of nonmethane hydrocarbon concentration. The following conclusions can be drawn:

- The worst storage tank module (L-22) had a specific emission rate of 85.4 $lb/hr/10^6\ ft^2$. This figure is much lower than either the covered API separator (L-49) with 1169 $lb/hr/10^6\ ft^2$ or the worst process area (near L-28) with $320\ \text{lb/hr}/10^6\ \text{ft}^2$.

- Since all of these sources are directly adjacent to the west boundary line, the predicted impacts should be roughly proportional to the specific emission rates. This is actually somewhat conservative, since the height of release of the storage tank emissions would be considerably higher than for a separator or for process fugitives. Therefore, it can be concluded that the specific impact of the worst storage module would be significantly less severe than the two worst points cited in this assessment.

- By examining the relative contributions of adjacent process sources to the predicted maximum and applying similar ratios to adjacent storage modules, it was determined that the inclusion of storage emissions in the modeling would not have significantly increased the estimated maximum concentration. It would, however, have greatly increased the area of impact in which relatively high concentrations of nonmethane hydrocarbons would occur.

The refinery layout may be even more critical than the complexity and the resulting overall emission rate, especially from the hydrocarbon species. Fugitive emissions are released near ground level, and thus are subject to much less dispersion than stack emissions. A refinery layout with process units right on the boundary line (such as the model used here) will show much higher hydrocarbon concentrations at the boundary than one with a buffer zone around the processing area.

The situation is further complicated when looking at individual species. For instance, a gas processing facility near the fence line would result in high concentrations of total hydrocarbons, but it would probably not cause any large source severity factors. On the other hand, a complex consisting of a reformer, an aromatics extraction unit, and a BTX fractionation unit would result in moderate to low total hydrocarbons, but they would probably result in high source severities for the aromatics components.

The choice of which type of dispersion model to use could affect the predicted pollutant concentrations significantly. None of the available models is perfect, and predicted maximum concentrations may vary from half to ten times (or more) the actual concentrations measured from a source. The use of the rural version of RAM to model a refinery is a conservative choice since the heat island effect of a refinery will tend to increase atmospheric diffusion. This should definitely be considered in interpreting these results.

The predicted impacts will also vary with meteorological conditions, as illustrated by sensitivity runs on the model. A 22 percent decrease in wind speed resulted in a 28 percent increase in predicted maximum ground level concentrations for total hydrocarbons. Use of the more stable atmospheric stability class D resulted in 3 percent higher predicted concentrations. While this sensitivity is interesting, the meteorological conditions used in the base case were firmly fixed by the "standard receiving atmosphere" for source severity calculations. The appropriateness of these conditions for predicting "real world" concentrations, however, is highly questionable.

The hydrocarbon component breakdown is also quite critical. Individual component source severity factors will vary in direct proportion with the predicted concentration of that component in the emitting source. There are fairly wide confidence intervals that should be applied to those component breakdowns. Component concentrations will vary from day to day with changes in feedstocks, operating conditions, etc. This effect is amplified by several orders of magnitude when discussing API separator emissions. The small number of samples on which the component analyses are based is insufficient to confidently average out such process variations.

There is a shortage of quantifiable toxicity data for the many organic compounds present in refinery processing. This makes it difficult to prepare a comprehensive environmental assessment. The accuracy of existing toxicity data is also questionable, and this effect is compounded by the transformation from TLV to an "acceptable pollutant concentration." Dividing the TLV by three to account for the difference between eight hours per day and continuous exposure assumes that the toxic effects are cumulative. For some compounds that is certainly true, but others require some critical concentration to be harmful and are easily assimilated by the body below that concentration. The safety factor of one hundred to account for the greater susceptibility of the general public is obviously arbitrary and therefore questionable. Any change in the acceptable pollutant concentration will produce an inversely proportional change in the calculated source severity.

Recognizing the high degree of uncertainty in the results, the following conclusions can be drawn:

- There is no certainty of public hazard resulting from the emissions of this hypothetical refinery.

- Conversely, there is no certainty that it does not create a hazard.

- If any hazard exists due to hydrocarbon species, the most likely species to cause problems would be the polynuclear aromatics.

- This approach to an environmental assessment of a generalized source is of limited value in providing specific information on whether steps need to be taken to further reduce emissions of a given pollutant.

- The results can be useful in indicating the relative impacts of various emission sources and species. For instance, API separators appear to pose more of a potential hazard than fluid catalytic crackers; polynuclear aromatics emissions appear to be more troublesome than benzene. Such relative ranking of emission sources and species can be useful in directing emphasis towards potential problem areas.

- If this approach were used to assess the impact of a specific plant, it might yield more useful results. The range of uncertainty would be much narrower because the input factors could be more firmly defined.

6.0 EFFECTS OF EXISTING AND POTENTIAL REGULATIONS AND POLICIES

This section will examine the effects of environmental regulations and permit policies on the emissions from petroleum refining. The first two subsections will deal with state and Federal regulations, respectively. The final section will address the effects of potential new regulations.

6.1 State Regulations

Existing facilities are regulated by the states, rather than by Federal standards. State regulations were obtained from the Environmental Reporter.[14] Standards for the South Coast and Bay Area regions of California are considered here with the state standards. Though some state standards were amended as late as 1979, most were adopted in the early 1970's.

There is a lot of disparity among the standards in some categories; the general trends which could be discerned are presented here along with notable exceptions. No attempt is made to describe the standards of the individual states *per se*.

All states are included even if they presently have no refineries. This should *not* be interpreted, however, to mean that all states have specific standards for all the categories included here. Some states have standards only for specific existing facilities; others have no standards except for support of federal standards. Some of the summaries presented below represent the standards of only a few states.

6.1.1 Particulate and Visible Emissions

Most states have specific standards for the maximum opacity and darkness of emissions. The strictest standard, and by far the most common, calls for a maximum opacity of 20 percent and a maximum darkness of No. 1 on the Ringlemann Chart. In some states these stricter standards apply only to new sources while existing sources are allowed an opacity of 40 percent and a darkness of No. 2 Ringlemann. In other states these more lenient standards apply to new and existing sources. One state allows 40 percent opacity for new sources and 60 percent for existing sources.

Some state standards specify either opacity or darkness, but not both. Exception to the above standards is sometimes allowed for the flue gases from catalytic cracking catalyst regeneration and fluid coking: these gases may be allowed 25 to 40 percent opacity where other gases are limited to 20 percent. In all states with visibility standards, provision is made for varying amounts of upset time.

Particulates are generally regulated by source. For process emissions in general, many state standards have a chart with pounds per hour allowable emissions versus tons per hour process weight, with all stacks considered collectively.

Again, catalytic cracking catalyst regeneration is sometimes considered separately. Although no exact comparison of the various standards can be made because of widely varying formats, the one pound per ton of coke burn-off standard of two states appears to be the most stringent. When a CO boiler is installed on the regenerator, an allowance is usually made for the added emissions from fuel-burning.

Particulate emissions from fuel-burning are also often considered separately. The stipulation is generally made that all fuel-burning at the facility is considered collectively. Standards range from 0.1 to 2.5 pounds of particulates per million Btu of heat input; a number of the standards stipulate a maximum of 0.6 lb/10^6 Btu or less. Some standards have varying maximums for different size units. One state standard specifies that afterburners must be used.

6.1.2 Sulfur Emissions

Several states limit SO_2 emissions from any source in a refinery to 500 ppmv; a common maximum is 2000 ppmv. One state limits total SO_2 emissions from the refinery to 10 percent of the sulfur in the crude; another limits total SO_2 emissions to 0.3 pounds per barrel of oil processed. Many states, however, consider separately the sulfur emissions from fuel burning and sulfur recovery. One state limits emissions of mercaptans specifically to 0.25 pounds per hour.

Most standards for SO_2 emissions from fuel burning are of two types. Some states limit the sulfur content of the fuel burned while others specify a maximum amount of SO_2 that may be emitted per million Btu of heat input. When the sulfur content of the fuel is limited, allowance is usually made for equivalent alternate means of SO_2 emission control.

Where the sulfur content of the fuel is limited, state standards stipulate maximums of up to 2.5 weight percent sulfur. Most maximums are 1.0 weight percent sulfur or less. Sulfur content of gaseous fuels (often specifically fuel gas) is expressed in grains of H_2S per dry standard cubic foot (gr/dscf). In this case the common maximum is 0.1 gr/dscf.

Allowable SO_2 emissions from sulfur recovery units are sometimes expressed in pounds of SO_2 per pound of sulfur processed. These allowances range from 0.004 to 0.12 lb SO_2/lb S. Several state standards contain a chart of allowable emissions versus sulfur input. One state allows up to 1000 pounds of SO_2 per hour. Limits of 500 to 2000 ppmv SO_2 are in some instances set specifically for sulfur recovery units.

Hydrogen sulfide emissions from sulfur recovery units are addressed by a few states. One state allows 0.3 pounds of H_2S per hour. One state allows 0.1 ppm H_2S and two others allow 10 ppm H_2S.

6.1.3 NO_x Emissions

State standards for the control of NO_x emissions from fuel burning are quite consistent. These standards, which normally apply only to units larger than 250 million Btu, allow gas-fueled units to emit 0.20 pounds per million Btu and liquid-fueled units to emit 0.3 pounds per million Btu. Solid-fueled units are allowed 0.7 pounds per million Btu. When different fuels are burned simultaneously, the applicable standard is determined by proration.

6.1.4 Carbon Monoxide Emissions

One state limits carbon monoxide to 200 ppmv in fuel-burning units larger than 10^7 Btu. All other CO standards are for the catalytic cracking catalyst regeneration and for fluid coking. Some states limit CO emissions from these sources to 500 ppmv; in some instances this limit applies only to new sources. One state allows existing sources to emit 20,000 ppmv CO, another allows the emission of 5 tons of CO per year.

The control method for CO emissions from catalyst regeneration and fluid coking is expressed specifically in several standards as combustion at 1300°F for 0.3 second in a direct flame afterburner or boiler with an indicating pyrometer located at eye level. Some, but not all, states with this stipulation allow the use of equivalent control measures. One state allows alternate control methods which remove at least 93 percent of the CO in the existing gas.

6.1.5 Hydrocarbon Emissions

Some standards stipulate that oil-water separators must be pressurized, have floating or double-deck roofs, have vapor recovery, or have an equivalent vapor control method. One state standard specified 85 percent control for wastewater separators, another 95 percent.

Most standards for pumps and compressors state simply that these must be equipped with mechanical seals or an equivalent control. Several states specify mechanical seals for rotating pumps and compressors and packing glands for reciprocating. Two states limit emissions from each pump and compressor to 2 cubic inches per 15 minutes; one standard limits leakage to 3 drops per minute.

A number of states specify that hydrocarbon waste from the vapor blowdown system be smokelessly flared or disposed of in an equivalent manner. One state specified that these emissions be controlled if they are more than 10 percent equivalent methane; another state sets a limit of 50 pounds per day.

Hydrocarbon emissions from catalytic crackers and fluid cokers are required by several states to be incinerated in a direct flame afterburner or boiler. One state allows 100 ppm equivalent methane or 8 pounds of hydrocarbons per hour before controls must be applied; another state allows 5 tons of hydrocarbons per year.

Other sources of hydrocarbon emissions are mentioned infrequently in state standards. Several standards specify that hydrocarbon emissions from condensers, hot wells and accumulators be incinerated, compressed, or equivalently controlled. One standard allows no hydrocarbon emissions from fuel burning; another specified 95 percent control of hydrocarbons from vacuum systems and from process unit turnarounds. One standard states that relief valves in pipes over one inch in diameter must be vented to vapor recovery or disposal, be protected by a rupture disc, or be maintained by an approved inspection system. In one standard, emissions from air blowing must be incinerated at 1400°F for 0.3 second or equivalently controlled.

6.1.6 Effects of State Regulations on the Environmental Impacts of Refineries

It is quite difficult to assess the effects of state regulations because of the great variety in standards. There is no doubt that significant emission reductions have been achieved over the last ten to fifteen years by virtue of these regulations. The model refinery used in this environmental assessment, however, already reflects the control technology required by the consensus of regulations for existing sources. Some reduction of the impacts could be expected if the refinery were located in one of the stricter states.

6.2 Federal Regulations and Policies

Federal regulations apply primarily to new or modified sources. These take the form of New Source Performance Standards (NSPS) and New Source Reviews required for permitting.

6.2.1 New Source Performance Standards

NSPS specific to refineries are contained in 40 CFR Part 60, Subpart J. These standards apply to fluid catalytic cracking unit regenerators, fluid cokers, sulfur recovery units, and fuel sulfur levels. Subpart D contains standards for fossil-fuel fired steam generators with a heat input greater than 250 million Btu. Subpart K includes standards for storage vessels containing petroleum liquids, but these are outside the scope of this study.

6.2.1.1 Particulate and Visible Emissions

Federal standards state that gases from fossil-fuel fired steam generators may not exhibit more than 20 percent opacity except for one 20-minute period per hour of not more than 27 percent opacity. These gases also may not contain more than 0.1 pound of particulate matter per million Btu of heat input from the fossil-fuel.

Gases from fluid catalytic cracking catalyst regeneration may not exhibit more than 30 percent opacity, except for one six-minute average reading per hour. These gases also may not contain more than 1.0 pound of particulate matter per 1000 pounds of coke burn off.

If the gases from the regenerator pass through an incinerator or waste heat boiler in which auxillary or supplemental liquid or solid fuel is burned, excess particulate emissions may be allowed. These excess emissions may be 0.1 pound or less per million Btu of heat input attributable to the added fuel.

6.2.1.2 Sulfur Emissions

When liquid fuels are used for steam generation, sulfur dioxide emissions must be no more than 0.8 pounds per million Btu of heat input. Any fuel gas which is burned in a combustion device must contain no more than 0.10 grain of H_2S per dry standard cubic foot or the sulfur dioxide emissions from the combustion device must be controlled in an equivalent manner. Flares for the combustion of process upset gas or fuel gas from relief valve leakage are exempt from this standard. Sulfur dioxide emissions from Claus plants must be limited to 0.025 percent (250 ppm) by volume on a dry basis at zero percent oxygen if emissions are controlled by an oxidation system (one which converts emissions to sulfur dioxide) or by a reduction system (one which converts emissions to hydrogen sulfide) followed by incineration. If emissions are controlled by a reduction system not followed by incineration, emissions from the unit may be 0.030 percent (300 ppm) reduced sulfur compounds and 0.0010 percent (10 ppm) hydrogen sulfide calculated as sulfur dioxide at zero percent oxygen on a dry basis. Reduced sulfur compounds include hydrogen sulfide, carbonyl sulfide, and carbon disulfide.

6.2.1.3 Carbon Monoxide Emissions

The standards for carbon monoxide states simply that no gases which contain more than 0.050 percent by volume (500 ppmv) carbon monoxide may be discharged to the atmosphere from a fluid catalytic cracking catalyst regenerator.

6.2.1.4 NO_x Emissions

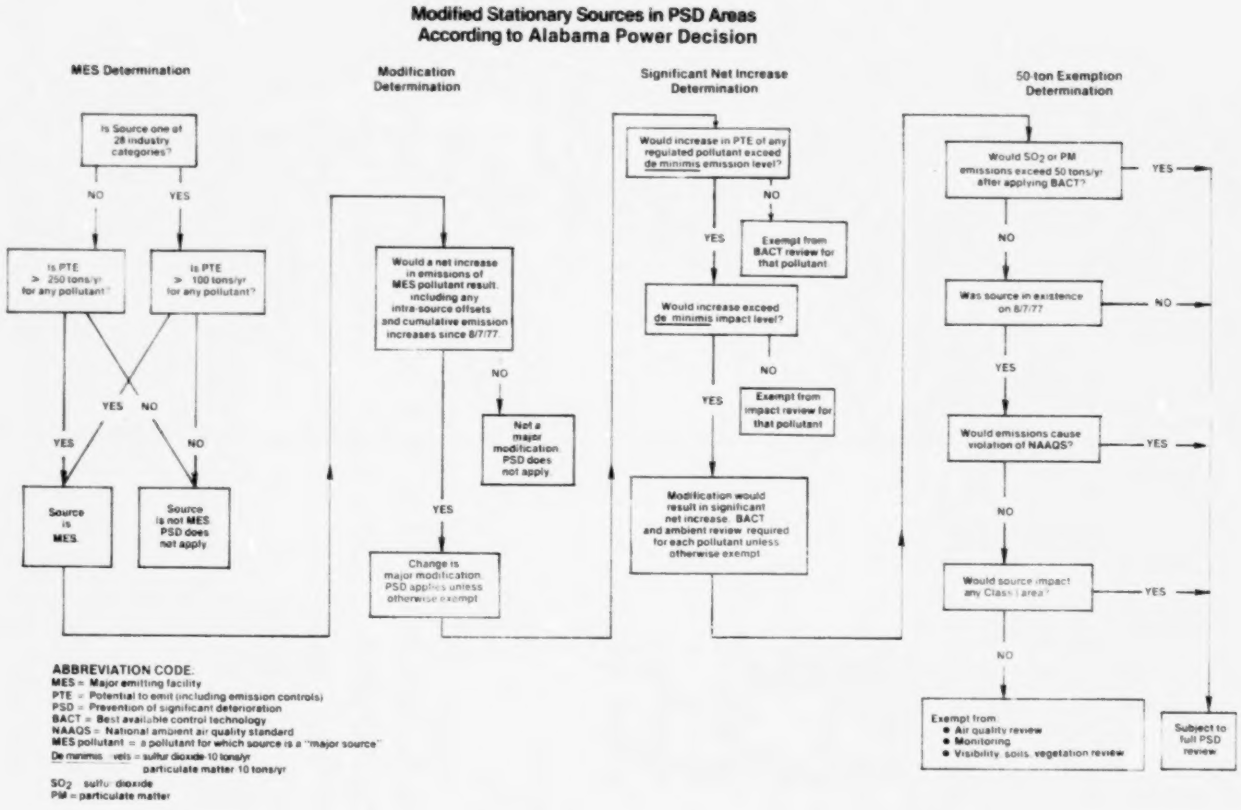
Allowable NO_x emissions from fossil-fueled steam generators vary with the type of fuel used. When gaseous fuel is used, emissions are limited to 0.2 pounds per million Btu of heat input. For liquid fuels the limit is 0.3 $lb/10^6$ Btu and for solid fuels 0.7 $lb/10^6$ Btu. When different fuels are burned simultaneously, the applicable standard is determined by proration.

6.2.2 New Source Review

The 1977 Amendments to the Clean Air Act emphasize the control of atmospheric pollutants from new or modified facilities by establishing a New Source Review (NSR) process. This is essentially a Federal permit to construct any major emission source. The review process can take one of two paths depending on whether or not the source is to be built in an area in attainment of the National Ambient Air Quality Standards (NAAQS). If so, the Prevention of Significant Deterioration (PSD) regulations apply. If not, then nonattainment regulations apply. Frequently, both paths must be followed, since attainment is judged on a pollutant-by-pollutant basis.

6.2.2.1 Prevention of Significant Deterioration

The PSD review process is a multilevel examination of the emission levels and air impacts of the new source. The overall process can best be illustrated by the flowchart shown in Figure D6-1. It would not be pertinent here to examine in detail the many applicability criteria which determine the level



MES Determination
Is Source one of 28 industry categories?
NO
YES
Is PTE > 250 tons/yr for any pollutant?
Is PTE > 100 tons/yr for any pollutant?
YES
NO
YES
NO
Source is MES
Source is not MES PSD does not apply
Modification Determination
Would a net increase in emissions of MES pollutant result, including any intra-source offsets and cumulative emission increases since 8/7/77
NO
Not a major modification PSD does not apply
YES
Change is major modification PSD applies unless otherwise exempt
Significant Net Increase Determination
Would increase in PTE of any regulated pollutant exceed de minimis emission level?
NO
Exempt from BACT review for that pollutant
YES
Would increase exceed de minimis impact level?
NO
Exempt from impact review for that pollutant
YES
Modification would result in significant net increase. BACT and ambient review required for each pollutant unless otherwise exempt
50-ton Exemption Determination
Would SO_2 or PM emissions exceed 50 tons/yr after applying BACT?
YES
NO
Was source in existence on 8/7/77
NO
YES
Would emissions cause violation of NAAQS?
YES
NO
Would source impact any Class I area?
YES
NO
Exempt from
● Air quality review
● Monitoring
● Visibility, soils, vegetation review
Subject to full PSD review

Modified Stationary Sources in PSD Areas According to Alabama Power Decision

ABBREVIATION CODE:
MES = Major emitting facility
PTE = Potential to emit (including emission controls)
PSD = Prevention of significant deterioration
BACT = Best available control technology
NAAQS = National ambient air quality standard
MES pollutant = a pollutant for which source is a "major source"
De minimis levels = sulfur dioxide 10 tons/yr
particulate matter 10 tons/yr
SO_2 sulfur dioxide
PM = particulate matter

Figure D6-1. PSD Applicability Chart

of review required. Suffice it to say that if a new or modified refinery (which is one of the 28 major industry categories) has the potential to emit more than 100 tons per year of any given atmospheric pollutant, and that represents a net increase in emissions since 8/7/77, and the net increase is greater than the "de minimis" level, the new or modified section must demonstrate the use of Best Available Control Technology (BACT).

BACT is defined as the level of emission control which gives the lowest emissions while taking into consideration the cost of control, energy efficiency, and technical feasibility. BACT must, therefore, be determined on a case-by-case basis to evaluate these effects. When an NSPS is available, this usually forms the minimum criteria for BACT. When no NSPS exists, then all possible methods of emission reduction must be catalogued. When one of these methods has been proposed as BACT for the new source, all methods giving lower emissions must be shown to be inappropriate in terms of cost, energy impact, or technical feasibility.

6.2.2.2 Nonattainment Requirements

The requirements for permitting a source which will emit significant levels of a pollutant for which the area is not in attainment of the NAAQS are quite stringent. First, the source must use the Lowest Achievable Emission Rate (LAER). It must then offset the resulting emissions by reducing emissions from another source in the area by a more than equivalent amount. There are additional requirements relating to other sources owned by the applicant and to assuring a net positive air quality improvement, but these are not pertinent to this discussion.

LAER is defined as the strictest control technology required for this type of source by any State Implementation

Plan (SIP), or the lowest emissions achieved by any operating source of the same type, whichever is more stringent, unless the owner or operator of the proposed source demonstrates that such limitations are not achievable. This does not take cost or any other side effects into account. It also recognizes the transfer of control technology from one type of source to another, if technically feasible.

The resulting emissions after LAER must be offset on a pollutant-by-pollutant basis by reducing emissions from other sources in the area. For nonreactive pollutants the offset must be from another source in the immediate vicinity. For NO_x and hydrocarbons, however, offsets can be obtained over a broader area. The offsetting emission reduction must be greater than the emissions from the new source, thus causing a new positive air quality improvement.

6.2.2.3 Effects of New Source Reviews on the Environmental Impacts of Refineries

The effects of the New Source Review process on the environmental impacts of refineries should be significant. Any new refinery permitted under this system should have much lower emissions than existing refineries. This would be particularly true in the area of hydrocarbon emissions, but it would also occur for NO_x and SO_2.

The NSR process will also discourage expansion in non-attainment areas, where the combined impacts of a heavily industrialized area have already caused a deterioration in air quality. If an expansion were to be made in such an area, it could only be done by achieving a greater than equivalent offset.

Thus, the impetus to build new facilities can provide the impetus to clean up older facilities. The net effect of these policies should be an improvement in existing air quality. In attainment areas, refinery construction and expansion will be limited by the constraints of PSD increments. Unlike the situation in non-attainment areas, few existing sources will be available to provide emission offsets which will be needed to allow growth once the PSD increment is consumed.

6.3 Potential Regulations and Policies

There are many standards and regulations currently under consideration that would have a significant impact on refinery emissions. It would be quite difficult to document all of these since many have not even been published as proposals at this time. Several examples will be discussed in this section to illustrate regulatory trends. Caution should be used in interpreting or applying these regulations since they are only proposed at this point, and they may be significantly modified before being adopted.

6.3.1 State Regulations

Only the new and developing standards for the Bay Area (San Francisco) and the South Coast (Los Angeles) regions of California are summarized here. Other regulatory agencies may be similarly updating their standards. Most of these new and proposed standards are concerned with the emission of hydrocarbons from refineries.

Two levels of control for SO_x emissions from catalytic cracker catalyst regeneration are being considered by the South Coast region, one of which is expected to become a standard by 1982. One proposed standard calls for replacement of the conventional catalyst with a newly developed catalyst which can reduce SO_x emissions by 90 percent without additional controls; the other proposes the addition of alkaline scrubbers for 90 percent control of SO_x. The South Coast region also proposes that the allowable sulfur contents of fuels be halved by 1982.

Many of the proposed standards are concerned with fugitive emissions, an area not emphasized by present standards. The South Coast region proposes that by 1980, leak rates, maintenance schedules, etc. for random hydrocarbon emissions be established. Pumps and compressors within three miles of the control center would be inspected every eight hours, all others every 24 hours.

The South Coast region also proposes that natural gas-fired control devices such as afterburners must have a stand-by fuel system for use during natural gas curtailment. By 1980, all relief valves would be vented to vapor recovery or disposal. By 1982, combustion modification and/or ammonia injection for control of NO_x would be required on heaters and boilers.

A Bay Area region standard which went into effect in December 1979, limits valve leakage to 10,000 ppmv VOC measured one centimeter from the leak. It is proposed that this standard be applied also to flanges.

By March 1980, emissions from condensers or vacuum-producing systems must be incinerated, compressed and added to fuel gas, or controlled equivalently. It is proposed that emissions from steam ejectors be similarly controlled.

Also, since March 1980, hot wells and/or accumulators associated with contact (barometric) condensers must be covered and the organic vapors either incinerated or contained and treated. It is proposed that this standard apply to the hot wells and/or accumulators associated with all condensers.

Emissions from process vessel depressurizing must, by 1980, be passed through a knockout pot to remove condensable hydrocarbons, then incinerated, flared, or compressed and added to the fuel gas. It is proposed that emissions from process vessel purging be similarly controlled.

Another Bay Area region standard effective March 1980, is similar to those in several other states: oil/water separators must have a solid cover, a floating pontoon or double-deck cover, 90 percent effective vapor recovery, or other approved control equipment.

6.3.2 Federal Standards

Petroleum refineries are among those industries for which New Source Performance Standards (NSPS) will be formulated in the near future. It is expected that within two to three years additional standards will be added to Subpart J of 40 CFR Part 60 and parts of the existing Subpart J may be revised. Additional standards may concern such emissions as SO_x from catalytic cracking catalyst regeneration and fugitive emissions.

6.3.3 Effects of Potential Regulations and Policies on the Environmental Impacts of Refineries

These proposed regulations will tend to bring more uniformity to the determination of BACT. They do not generally increase the stringency of measures already required through the

New Source Review process. If other states follow California's lead in upgrading their SIP's, however, the allowable emissions from existing refineries could be greatly reduced. Such stringency in state regulations may or may not be warranted, depending on the magnitude of any air quality problems in the specific state.

7.0 EFFECTS OF NEW AND DEVELOPING TECHNOLOGY

Although petroleum refining is considered a mature technology area, it is constantly undergoing a process of improvement. The environmental impacts of refineries will be reduced in the future through new developments in both process technology and emission control technology.

7.1 Process Technology

Process technology in petroleum refining has continually evolved to meet the demands of the end-use sector. Some of the current evolutionary trends in refining include the shift to produce lead-free gasoline, increased use of hydrodesulfurization to achieve lower fuel sulfur contents, and a push for greater energy efficiency. Some of these trends will tend to aggravate emissions while others will reduce them.

The production of lead-free gasoline requires significantly more processing in units like catalytic reformers, alkylation units, and isomerization units. While the units are not major emitters, they do contribute to fugitive emissions and emissions from combustion sources. Since there is a decrease in gasoline range yields with this type of processing, more crude must be charged to maintain the same gasoline production. This will cause slight increases in emissions across the board. Much of this effect is now behind us, but a phase-down of gasoline pool lead content will cause continued emissions increases.

Sulfur levels in many fuels are being regulated downward. This will require an increased use of hydrodesulfurization to achieve these low sulfur levels, which will, in turn, increase the load on Claus plants and tail gas treating units. The hydrogen demand will also begin to exceed that provided by catalytic reforming, and thus require construction of hydrogen plants. Both of these effects will tend to cause an increase in refinery emissions unless countered by more effective control technology.

The trend toward greater use of energy conservation will tend to reduce the emissions from combustion sources. The recovery of process heat and the use of intrinsically more efficient processes will reduce the heat required from process heaters and steam boilers. Since the emissions from combustion equipment are proportional to the fuel burning rate, this should result in an emission reduction.

7.2 Emission Control Technology

New and improved emission control technology will continue to appear in petroleum refining. Significant reductions could be achieved by widespread application of recently developed technology, such as covers for API separators, scrubbers for flue gas from fluid catalytic cracking, and combustion modifications to reduce NO_x. These effects will be complemented by progess on developing technologies like the fluid cracking catalyst which adsorbs SO_x from the regenerator.

One area with great potential for improved technology is in fugitive emission control. The manufacturers of seals, packing, and gaskets for process equipment have designed their products to meet the users' needs. Up until now, those needs have been to limit product loss and maintain safe operation. No one was aware or concerned about "low level" fugitive vapor leaks which could not be detected visibly. Fugitive emission regulations will provide the incentive to develop more effective seals, packing, etc., and will result in lower emissions and lower costs for monitoring and maintenance programs.

8.0 CONVERSION FACTORS

To Convert From	To	Multiply By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
$lb/10^6$ Btu	g/Mcal	18.0
$grain/ft^3$	g/m^3	2.29
$gal/10^6 ft^3$	$\ell/10^6 m^3$	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mg/ℓ	119.8

REFERENCES

1. Serth, R.W., et al., Source Assessment: Analysis of Uncertainty, Vol. II: Application to Air Source Assessment Program, EPA-600/2-77-107, EPA, Research Triangle Park, N.C., 1977.

2. Powell, D., et al., Development of Petroleum Refinery Plot Plans, EPA-450/3-78-025, EPA, Research Triangle Park, N.C., June, 1978.

3. Environmental Protection Agency, Office of Air Quality Planning and Standards, Compilation of Air Pollutant Emission Factors, AP-42, Third Edition plus Supplements, Research Triangle Park, N.C.

4. Wall, J., Gas Processing Handbook, Hydrocarbon Processing, April, 1975.

5. Wetherold, R.G., and Provost, L.P., Emission Factors and Frequency of Leak Occurrence for Fittings in Refinery Process Units, EPA-600/2-79-044, EPA, Research Triangle Park, N.C., February, 1979.

6. Bombaugh, K. J., et al., Sampling and Analytical Strategies for Compounds in Petroleum Refinery Streams, Vol. II. Radian Corporation, Austin, Texas, September, 1975.

7. American Petroleum Institute, Medical Research Report #EA-7103, Petroleum Asphalt and Health. Reinhold Publishing Company, 1966.

8. EPA, Office of Air and Waste Management, Guideline on Air Quality Models, Research Triangle Park, N.C., 1978.

REFERENCES (Continued)

9. Turner, B. Workbook of Atmospheric Dispersion Estimates, No. AP-26 EPA, Office of Air Programs, Research Triangle Park, N.C., 1969.

10. Larsen, R. A Mathematical Model for Relating Air Quality Measurements to Air Quality Standards EPA, Office of Air Programs, Research Triangle Park, N.D., 1971

11. Novak, J.H., et al. An Efficient Gaussian-Plume Multiple-Source Air Quality Algorithm APCA Journal, 26(6), June 1976.

12. Gifford, F. and Hanna, S. Urban Air Pollution Modeling. In: Proceedings of the Second International Clean Air Congress, H. Englund and W. Beery, ed. Academic Press, New York, 1971, pp 1146-1151.

13. Thayer, D.S. and Koch, R.C. Validity of the Multiple-Source, Gaussian Plume Urban Diffusion Model Using Hourly Estimates of Input, Preprint Volume of the Conference on Urban Environment and Second Conference of Biometeorology. American Meteorological Society, Boston, Mass., 1972.

14. Environment Reporter, State Air Laws, Bureau of National Affairs, Inc., 1231 Twenty-fifth Street, N.W., Washington, D.C.

APPENDIX E:

CONTROL TECHNOLOGY REVIEW AND EVALUATION

APPENDIX E: CONTROL TECHNOLOGY REVIEW AND EVALUATION

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1.0 INTRODUCTION

1.1 Objectives

In this appendix, techniques for controlling atmospheric emissions are presented. These techniques include controls that are typically used in the refining industry, controls used in some areas in the refining industry that may be applicable to other areas, and controls used in other related industries that could be applied to similar emission sources in the refining industry. The effectiveness, cost, energy requirement, and applicability of some of the emission control technique are presented. Techniques for controlling fugitive emissions and process emissions are included in this appendix. Fugitive hydrocarbon emissions may be caused by leaks from process equipment sealing devices such as pump and compressor seals, valve seals, and flange gaskets or may be caused by atmospheric exposure of hydrocarbon-containing substances that result in evaporative hydrocarbon emissions. Fugitive particulate emissions are generally the result of wind action on unpaved areas and storage piles. Process emissions are released to the atmosphere via a stack, flue, or vent duct.

Control techniques or control technologies include equipment controls, process controls, feedstock and fuel controls, and work practice controls. The term equipment controls pertains to the substitution or modification of unit operations hardware or addition of emission control hardware. Emission control hardware can generally be described as device which capture, collect, and/or destroy pollutants. Substitution or modification of unit operations hardware can be characterized as methods that reduce the likelihood of emissions from the unit operations process equipment. Process controls include any changes in operating parameters that result in a net decrease in emissions. Feedstock and fuel controls consist of modifications such as treating processes to remove pollutants before utilization and substitution of materials containing no pollutants or lower levels of pollutants. Work practice controls consist of maintenance and housekeeping activities that either reduce the emission potential of a source or that identify emitting sources and subsequently reduce the emission rate from the source.

1.2 Scope

Discussions of emission sources and emission controls are limited to the battery limits of process units in refineries. Emissions from transfer facilities, storage vessels, or other auxiliary processes such as electricity generation are not included. Coal combustion is not discussed as a fuel substitution alternative because of its complexity and its economically questionable application to petroleum refining. Electricity/steam cogeneration is not considered as a fuel substitution alternative. Petroleum based fuels and natural gas are considered as fuel substitution alternatives.

Controls for fugitive emissions discussed in Section 2 include equipment and work practice controls. Equipment controls for process emissions are discussed in Section 3, and process, fuel, and feedstock controls for process emissions are discussed in Section 4. Controls for fugitive emission sources are generally applicable to a particular source type (valve, pump, etc.) regardless of the type of process unit.

Fugitive emission controls are, therefore, discussed by source type. Process emission controls are discussed on the basis of the type of process unit, because of the differences in emissions and controls between processes.

2.0 CONTROL OF FUGITIVE EMISSIONS

2.1 Sources of Fugitive Emissions

Sources of fugitive emissions include process equipment that can "leak" hydrocarbons such as valves, flanges, pumps, compressors, agitators, and relief valves. Fugitive emissions may also result from atmospheric exposure of hydrocarbons from sample purging, drains, wastewater systems, and cooling towers. Unpaved roads and outdoor storage piles may be sources of fugitive emissions of particulate matter. Because the primary emphasis of the sampling effort was measurement of hydrocarbon emissions, these particulate emission sources are not discussed. Controls for these two types of fugitive emission sources are practiced in many other industries and include ordinary techniques such as watering or paving of roads and covering or coating storage piles.

Solid wastes generated in refineries may also be a source of fugitive emissions of hydrocarbons, particulates, or other pollutants depending on methods for handling and disposal of the solid wastes. A brief description of sources of solid wastes and disposal alternatives is included in Section 2.2.10.

2.2 Control Technology for Fugitive Emissions

For all of the sources that may "leak" hydrocarbons (valves, pumps, etc.) one control option is a leak detection and repair strategy. This type of work practice emission control is described in total for valves. For each of the succeeding leak sources, only the specific features that would be different for that type of source are described. Various types of equipment controls may be applicable to more than one source such as mechanical seals for pumps, compressors, and agitators. In these cases, reference may be made to a preceding description of the control technology.

The descriptions of fugitive emission control technology are presented for each type of emission source (valve, pump, etc.). The order of presentation is such that sources with similar types of controls are discussed in sequence. The relative contribution of source types for a hypothetical refinery is presented in Section 2.7.3 of Appendix B of this report.

Three levels of control are described for each source. Existing controls are those in general refinery use, although the extent of application may be variable. Available control technology may be used in some areas of the refining industry due to regulatory or other constraints, and control technology transfer includes any types of emission controls that have been applied to similar types of emission sources in other industries.

2.2.1 Valves

Valves can leak hydrocarbons through the junction where the activating stem penetrates the valve body. Excessive leakage from this junction is generally prevented by a packing gland or a pressurized grease seal. If a valve is operated with one side of the valve seat open to the atmosphere, such as for draining or sampling operations, hydrocarbons may leak through the valve seat. The following discussions pertain to these two potential leak sources for valves. Recent review articles are available that describe the overall features and functions of valves in detail.[1]

Table E2-1 contains the approximate distribution of refinery valves screened by Radian within the battery limits of major process units during the thirteen refinery sampling programs. The distribution of each type of valve is shown for manually operated and automatically controlled service categories. The Radian survey results indicate that 88 percent of all refinery valves screened were either manual gate valves (65 percent) or control globe valves (23 percent). Figure E2-1 shows the internal features of the various types of valves. Check valves are not discussed because they do not have a potential leak junction, and relief valves are discussed in Section 2.2.6.

2.2.1.1 Existing Controls for Valves

Existing controls for valves include the valve stem seal, inspection and maintenance practices, and closure of the atmospheric side of open-ended valves.

Valve Stem Seals--The valve stem seal is designed to prevent leakage of the contained fluid and is therefore a fugitive emission control. All gate, globe, and butterfly valves screened by Radian had a packed gland stem seal. These packed stem valves represent approximately 94 percent of all refinery valves. Plug valves typically have a grease-lubricated, tapered plug to prevent leakage. Grease may be added periodically to prevent leakage and to assure proper operation of the plug valve.

Packed stem seals consist of a stuffing box that surrounds the stem, rings of compliant packing material in the annular space, and a gland or follower that is used to compress the packing against the stem to form a seal. Figure E2-1 shows packing nuts that force the gland against the packing, but many valves may have bolts or studs that pass through the gland in

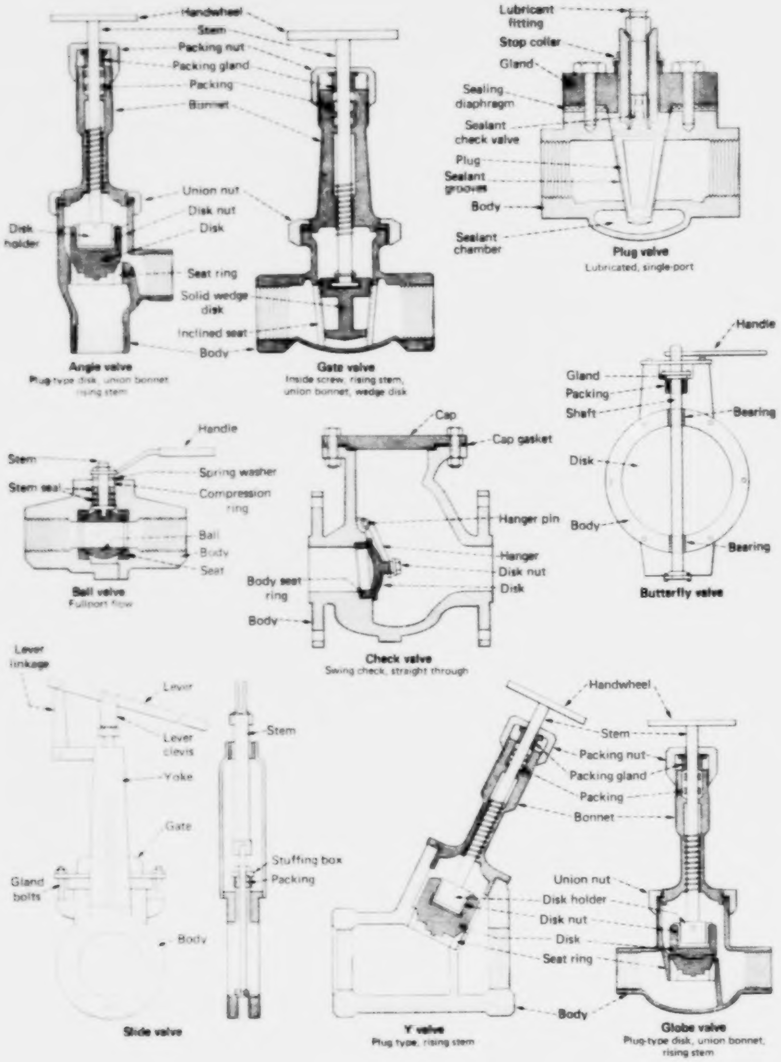
Handwheel
Stem
Packing nut
Packing gland
Packing
Bonnet
Union nut
Disk nut
Disk
Disk holder
Seat ring
Solid wedge disk
Inclined seat
Body
Angle valve
Plug-type disk, union bonnet rising stem
Gate valve
Inside screw, rising stem, union bonnet, wedge disk
Lubricant fitting
Stop collar
Gland
Sealing diaphragm
Sealant check valve
Plug
Sealant grooves
Body
Sealant chamber
Plug valve
Lubricated, single-port
Handle
Gland
Packing
Shaft
Bearing
Disk
Body
Bearing
Butterfly valve
Handle
Stem
Stem seal
Spring washer
Compression ring
Ball
Body
Seat
Ball valve
Fullport flow
Cap
Cap gasket
Hanger pin
Hanger
Disk nut
Disk
Body seat ring
Body
Check valve
Swing check, straight through
Lever linkage
Lever
Lever clevis
Yoke
Gate
Gland bolts
Body
Stem
Stuffing box
Packing
Slide valve
Handwheel
Stem
Packing nut
Packing gland
Packing
Bonnet
Union nut
Disk holder
Disk nut
Disk
Seat ring
Body
Y valve
Plug type, rising stem
Globe valve
Plug-type disk, union bonnet, rising stem

Figure E2-1. Process Valves

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order to permit packing adjustment by tightening nuts on the bolts or studs. Valve packing may lose its resiliency due to age or overtightening, and replacement of the packing is then required.

The fluid may be further prevented from diffusing through stranded type packing by dispersion of lubricant through the packing. The lubricant also alleviates galling, heating, and scoring of the stem or shaft. In most cases, a lubricant must be compatible with the packing and the working fluid. In refining, this lubricant might be a silicone oil, a petroleum grease, or a TFE or graphite dispersion in an oil or grease.

Lubricants are often present in the coils or rings of packing as received. They may also be introduced into the gland through a "grease" fitting which passes lubricant into a "lantern ring" positioned in the stuffing box. A "lantern ring" replaces a ring of packing. It is grooved to allow free flow of lubricant completely around the stem or shaft. As packing wear or lubricant loss occurs, the packing gland is tightened and/or additional lubricant is injected to provide a tight seal face and relatively impervious packing.

Table E2-2 shows the diversity of valve packing materials used alone or in combination.[1] Most of these materials may be purchased in coils or in preformed rings. They may be solid or stranded and may have a round, square, "U," or chevron cross-section.

Inspection and Maintenance--All refineries have operating practices that require repair of any leaks detected. These practices are primarily aimed at preventing fires or other safety hazards that could result from large amounts of hydrocarbon leakage. The leak detection methods used are generally

TABLE E2-2. PACKING MATERIALS - PROCESS VALVES

Packing Material	Form	Use	Temperature
Flexible, all metallic	Spiral wrapping. Thin ribbons of soft babbit foil.	Valve stem packing	Up to 450°F.
Flexible metallic packing (aluminum).	Spiral wrapping. Thin ribbons of soft annealed aluminum foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Flexible metallic packing (copper).	Soft annealed copper foil loosely around a small core of pure dry asbestos.	Hot oil valves, diphenyl valves.	Up to 1000°F.
Long-fiber pure asbestos and fine lubricating graphite (nonmetallic).	Graphite special long-fiber asbestos binder.	Extreme resilience.	Up to 750°F.
Closely braided asbestos yarn; top jacket reinforced with Inconel wire; core: long fiber asbestos.	Spools, die-formed rings.	High-temperature valves.	Up to 1200°F.
Pure asbestos yarn with an Inconel wire insert around a resilient asbestos core impregnated with graphite.	Spool form, die formed.	Valve stem for air, water, steam and mineral oil.	Stuffing box temperature up to 1200°F.
Twisted long fiber Canadian asbestos.	Spool form, die formed.	Valves handling, high and low pressure steam.	Up to 500°F.

(Continued)

TABLE E2-2. Continued

Packing Material	Form	Use	Temperature
Asbestos, graphite and oilproof binder.	Spool form, die formed.	Shutoff valves.	Up to 550°F.
Solid, braided TFE.	Coil, spool, ring.	Valve shaft for highly corrosive service.	100°F to 500°F.
Braided asbestos with complete impregnation of TFE.	Coil, spool, ring.	Valve stems in mild chemical or solvent service.	100°F to 600°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite and asbestos.	Coils, spools.	Valve stems, steam, air, mineral oil.	Up to 1200°F.
Braided of high quality wire-inserted asbestos over a loose core of graphite.	Coils, spools.	Stainless-steel valve stems, air, steam, water.	Up to 1200°F.
Braided of long-fiber Canadian asbestos yarn each strand impregnated with heat-resistant lubricant.	Coils, spools.	Valves for steam, air, gas and mild chemicals.	Up to 550°F.
Long-fiber Canadian asbestos yarn, each strand treated with a synthetic oilproof binder and impregnated with dry graphite.	Coils, spools.	Refinery valves.	To 750°F.

(Continued)

TABLE E2-2. Continued

Packing Material	Form	Use	Temperature
Braided/overbraided, wire-inserted, white asbestos packing impregnated with a heat-resistant lubricant.	Coils, spools.	Valve stems, for valves handling steam, air, gas, cresylic acid.	Up to 750°F.
Braided white asbestos yarn impregnated with TFE suspensoid.	Coils, spools.	Valve stems.	100°F to 600°F.
Braided or bleached TFE multifilament yarn.	Spools, coils.	Valve stems for highly corrosive liquids.	12°F to 500°F.
Braided TFE multifilament yarn impregnated with TFE suspensoid.	Spools, coils.	Valve stems for corrosive chemicals, solvents, gases.	120°F to 600°F.
Asbestos jacket, braided over a dry-lubricated plastic core of asbestos graphite and elastomers.	Spools and coils.	Valve stems, for valves handling superheated steam, hot gases.	Up to 850°F.

Source: Reference 1.

the eyes, ears, and nose of employees in the process unit. Radian's emission sampling program revealed that many leaks from valves and other sources may not be detected by sight, hearing, or smell. It is also a common refinery practice to lubricate valves and tighten packing glands periodically.[2,3] For some valves, the packing can be replaced while the valve is in service. These practices are generally applied in order to maintain the operability of the valves, rather than for fugitive emission control. Malfunctioning valves are usually replaced or rebuilt during process unit turnarounds, but malfunctioning is not usually defined as a valve with excessive fugitive emissions.

Open-Ended Valves--Open-ended valves may be used for draining, venting, or sampling operations. In addition to fugitive emissions from the stem seal, the valve seat may be a source of fugitive emissions. In order to prevent emissions through the seat, the open-end can be sealed with a cap, plug, blind flange, or a second valve. In most refineries, sampling connections have two valves in series (double block and bleed). This provides a second valve seat to resist emissions of the process fluid to the atmosphere. After operations requiring flow through the valves, the upstream valve should be closed first in order to avoid trapping hydrocarbons between the two valves, which would be essentially the same as one open-ended valve. Some refineries also seal drain and vent valves with caps, plugs, or blind flanges when the valves are not in use.

Effectiveness of Existing Controls--The absolute effectiveness of existing controls is reflected in the emission factors shown in Section 2.6 of Appendix B of this report. These emission factors were derived from test data collected from a broad cross-section of thirteen refineries, and all levels of the existing types of control were included. The relative effectiveness of existing controls - whether or not one type of packing or maintenance schedule is better than another - cannot be determined from available data. The costs of any type of increased emission control, such as using caps for open-ended valves or more frequent maintenance schedules, would be at best partially offset by the value of the product losses saved.

2.2.1.2 Available Control Technology for Valves

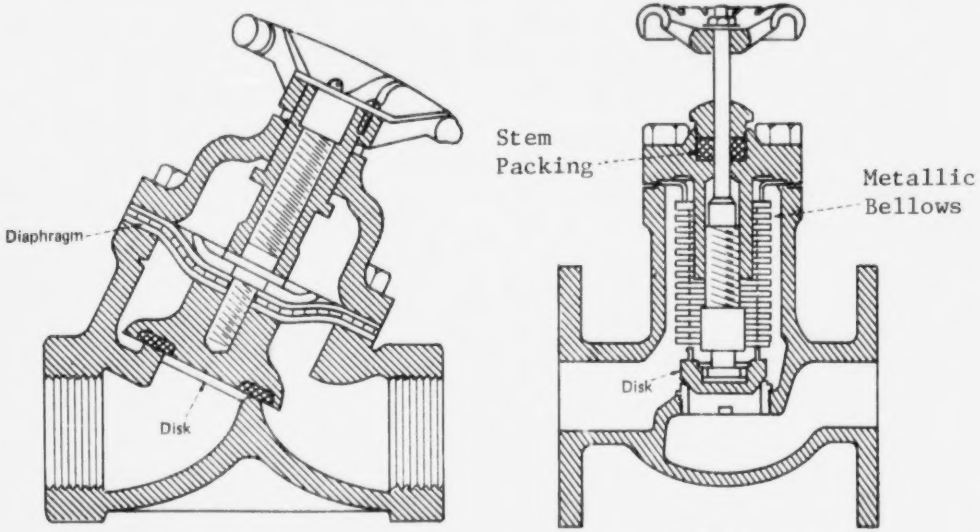
Leak detection and repair programs are the available controls for valves. For future construction, process design evaluation could be used to eliminate any superfluous valves. Leak detection and repair programs are a regulatory requirement in some areas. The frequency of application of leak detection and repair will probably increase due to additional regulatory requirements and due to the increasing value of the products lost as fugitive emissions.

Leak detection and leak repair programs consist of strategies to identify sources that are leaking significant amounts of hydrocarbons and methods to reduce or eliminate the leakage. At a specified interval, each valve would be checked with a portable hydrocarbon detector. The probe of the detector would be traversed around the potential leak areas (stem, gland, plug). If a predetermined hydrocarbon concentration limit (action level) were exceeded, the valve would be repaired. The repair could consist of tightening the packing, injecting grease, replacing the packing, or replacing the valve. During repairs such as tightening or greasing, the hydrocarbon detector should be used to permit assessment of the effect of the repair attempt. This type of repair is called "directed" maintenance.

Effectiveness--In the limited valve repair study conducted by Radian, the average emission reduction immediately after "directed" maintenance was 91 percent. The emission reduction after "undirected" maintenance was 54 percent, where "normal" maintenance procedures were used without using the hydrocarbon detector to optimize emission reduction at the time of maintenance. The detailed test results of the maintenance study are shown in Section 6.0 of Appendix B of this report. Data on the long-term effects of maintenance are not available.

In addition to "normal" maintenance procedures such as tightening or greasing, injection of sealing fluids may be used to reduce fugitive emissions. The valve body could be drilled and tapped, and sealing fluid could be injected in order to seal the leak. The long-term effects on emission reduction and valve operability are not known. For some control valves, operating procedures may prohibit excessive in-service adjustment in order to prevent malfunction of vital process control valves.

The required frequency of leak detection is dependent on the rate of recurrence of repaired leaks and the rate of occurrence of new leaks. The selection of an appropriate action level is dependent on the demonstrated ability to repair leaks of a given magnitude. Radian test results show that the smaller the initial leak rate, the more likely it is that repair efforts will increase rather than decrease the leak rate (Appendix B, Section 6.0). The other factors that influence the overall effectiveness of a leak detection and repair program is the average leak rate after repair. Limited test results show that for some valves the leak can be completely eliminated but for some others, the leak may be only slightly reduced or even increased by the attempted repair. Because these factors


Diaphragm
Disk
Stem Packing
Metallic Bellows
Disk

Diaphragm Bonnet Seal

Bonnet Bellows Seal

Figure E2-2. Globe Valves With Isolated Stem Seals
Reprinted by special permission from CHEMICAL ENGINEERING[6]

The diaphragm material in the diaphragm valve limits operation to about 50 psi pressure differential.[7] This type valve has definite limitations in refinery use. It would fail catastrophically upon overheating of the elastomer diaphragm, so it should not be used in hydrocarbon service where a fire could be fed by its failure. The bellows-sealed valve, because of the corrosion and fatigue failure potential of the bellows, is subject to combined temperature-pressure-corrosivity stress. Its usage is best defined by the valve manufacturer. Bellows-sealed valves should have stem seal packing as back-up protection against bellows failure.

Because use of these special valve stem seals will probably be limited, the impact of their use on emission control should also be limited, as would any economic impact. No primary energy cost would result from substitution of a very limited number of packless valves for conventional packed-stem, bonnet-sealed valves.

Diaphragm and bellows valves are approximately 1.5 to 3.7 times as expensive as gate valves according to the CARB report.[8] Another source estimated that bellows valves might cost 10 to 20 times as much as packed-stem valved, but would have a lower cost multiple if purchased in volume.[9]

2.2.2 Flanges

Flanges are paired junctions between sections of pipe and pieces of equipment. They are sealed against leakage by the tightening of bolts or studs which compress a flat gasket between the flat faces of the mating flanges, or compress an "o" ring set in the grooved faces of special flanges. The most common flanges have raised faces to accommodate tightening of the bolt and centering of the gasket, as shown in Figure E2-3. Typical gasket materials are asbestos composition or spiral, metal strip-reinforced asbestos or TFE. "O" rings may be made of neoprene, TFE or soft metals, depending upon temperature and pressure limits.

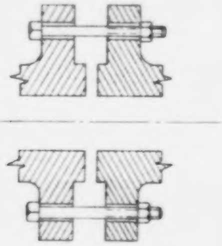


Figure E2-3. Raised-face Flange (gasket not shown).

The results of the refinery sampling program showed that flanges have a very low emission factor, and even though there are many of them, their overall contribution is small. The only real controls available for flanges are leak detection and repair programs. If a leak is found, the only repair options are tightening the flange bolts or injection of a sealing fluid, since most flanges cannot be isolated from the process in order to permit gasket replacement. Because of their lower emission contribution, flanges would not warrant as frequent leak testing as other sources such as valves.

2.2.3 Pumps

Pumps can leak hydrocarbons at the junction of the shaft and body of the pump. Two basic types of seals are used to prevent massive leakage from this junction. Packed seals can be used on pumps with reciprocating or rotating shaft motion, and mechanical seals are applicable only to rotating shafts.

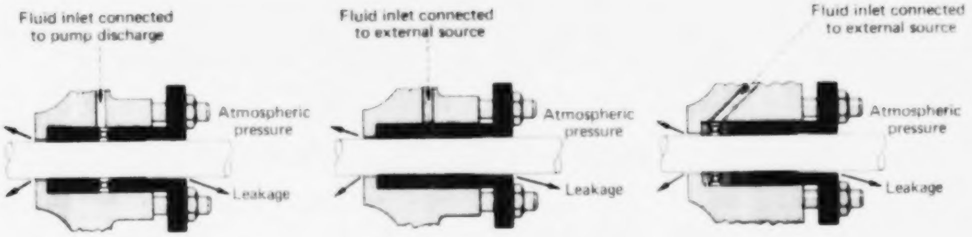
2.2.3.1 Existing Controls for Pumps

The two types of existing controls for pumps are the pump seal itself, and inspection and maintenance of the pump seal. The packed seal and mechanical seal resist leakage of the pumped fluid by different mechanisms, and are described separately.

Packed Seals--The packed seal, Figure E2-4, is used to seal both rotary and reciprocating shafts against leakage of liquid from the "working fluid" end of the shafts to the atmosphere. Compressed packing in the stuffing box forms a contact seal against the moving drive shaft. Friction resulting from this contact requires that either the working fluid be allowed to leak from the stuffing box housing the packed shaft, or a supplementary liquid be introduced to remove frictional heat.

As Figure E2-4 shows, a packed seal system may require injection of heat removal fluid, which is distributed in the stuffing box by a slotted "lantern ring." The fluid may be injected to not only remove heat but also to (1) seal the shaft for vacuum service, (2) flush the stuffing box lip of slurry solids, (3) provide a high flush rate to prevent shaft damage from abrasives, or (4) prevent hazardous materials from being released to the atmosphere.

Packings for the compression-type seals shown in Figure E2-4 may be solid or braided, twisted or ribbon-form (the latter form in graphite only). They may be obtained in continuous rolls or preformed rings. The shape is not restricted


Fluid inlet connected to pump discharge
Atmospheric pressure
Leakage
Fluid inlet connected to external source
Atmospheric pressure
Leakage
Fluid inlet connected to external source
Atmospheric pressure
Leakage

a. Negative-suction service
To assure fluid in stuffing box

b. Slurry service
Clean liquid flush to lantern ring

c. Abrasive service
Clean liquid flush to lantern ring

Figure E2-4. Packed Seals
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to the square cross-sections used for illustration. The cross-section may be round, plaited or braided square or rectangular, ot it may be "u," "v," or chevron-shaped. The last three shapes typically maintain their seal against a shaft after minimal initial tightening of the gland, and require little adjustment thereafter. For this reason, these packings are referred to as "automatic" packings.

Service limits for selected packings are found in Table E2-3. Note the inclusion of asbestos in the table. Asbestos is an OSHA-controlled substance, but is deemed safe when (1) modified by the lubricants and/or bonding agents impregnating the packings, and (2) cut for fitting purposes rather than sawed or abraded. Under moderate conditions the trend in braided packings is away from asbestos and toward TFE because of the latter's low coefficient of friction and its chemical inertness.

Lubricants for packings include the following substances:

- Mica and talc - high friction value lubricants, but do not discolor product.

- Graphite - the most common lubricant. May contribute to electrolytic or galvanic corrosion, especially in high-pressure steam service. May color product.

- Molybdenum disulfide (MoS_2) - dry lubricant similar to graphite. Does not cause electrolytic corrosion. Prevents metal galling. Oxidizes above 650°F and is then no longer a lubricant.

TABLE E2-3. SERVICE LIMITS FOR SELECTED MECHANICAL PACKINGS[a]

Packing	Maximum Temperature[b] (°F)	Pressure at Maximum Temperature[b] (psig)	Maximum Pressure[b] (psig)	Temperature at Maximum Pressure[b] (°F)
Asbestos/TFE	500	50	200	100
TFE (lubed)	500	50	200	100
Asbestos/Graphite	400	50	250	100
Graphite-Fiber	1000 (600)[c]	50	350	300
Graphite-Ribbon	1000 (600)[c]	50	350	300
Lead	350	50	400[d]	100
Aluminum	800 (500)[d]	50	400[d]	200

[a] Basic data: 2-in shaft, 3550 rpm. Controlled leakage for 720 h. Pumped liquid is water. Assumes maximum ΔT of 100°F (50°F for flax) due to shaft friction. Satisfactory results can be expected by using these maximum limits and following FSA (Fluid Sealing Assn.) Test Procedure #1. Source: Reference 10.

[b] Temperature is product temperature; pressure is stuffing-box pressure.

[c] Larger number is nonoxidizing environment; smaller number is oxidizing environment.

[d] Assumes rings are die-formed.

- Hydrocarbon type lubricants (greases, tallow, petroleum oils) - have low chemical resistance; carbonize at elevated temperatures; may be soluble in product being pumped.

- Tungsten disulfide - not as good a lubricant as MoS_2 or graphite, but is stable to 2400°F.

- TFE - a significant factor in lubricants as well as in woven packings. Temperature limit between 400°F and 500°F.[10] TFE is inert to all common chemicals except molten alkali metals and some rare, halogenated compounds.

- Silicone oils - temperature-resistant, corrosion-resistant oils are often injected at the lantern ring in stuffing box. Some silicones will oxidize and hence lose lubricating properties.

Mechanical Seals--The mechanical seal in its many forms is the predominant pump seal today. Contrary to the broader application of packed seals to both rotating and reciprocating shafts, however, mechanical seals are used only on rotary shafts. Mechanical seals may be used to seal both pump and compressor shafts, but are more universally applied to pumps, specifically centrifugal pumps. The American Petroleum Institute (API) recommends mechanical seals as particularly advantageous for hydrocarbon emission control in the following cases:[11]

- "... more-or-less continuous pumping of products having a Reid Vapor Pressure of 5 pounds per square inch..."

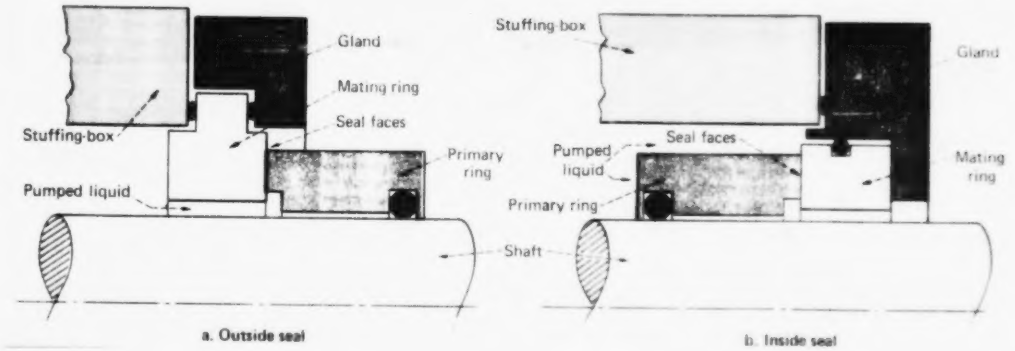
- "... when fluids are under substantial pressure and when the pump or compressor is in continuous service. For pumps operating on stand-by service either packed or mechanical seals may be used."

At the time of the Los Angeles County, California, study twenty years ago, mechanical seals made up only 42 percent of the seals in use there.[12] In Radian's survey approximately 82 percent of the screened refinery pump seals were mechanical.

Mechanical seals are prefabricated assemblies which shift the point of wear from the drive shaft, as with packed seals, to easily-replaced pairs of rings. One of the rings is attached to the pumpshaft, and the other to the gland plate or its equivalent. Seal faces are perpendicular to the shaft and are typically lapped to a precise flatness that accounts for their typically low leak rate when carefully installed and started up.

Single Mechanical Seals - A single mechanical seal may be an outside seal or an inside seal depending on whether the primary ring is outside or inside the stuffing box housing. Figure E2-5(a) depicts an outside seal; Figure E2-5(b) represents an inside seal. In the majority of cases, an internal seal is used; the primary ring is attached to the shaft, and the mating ring to the gland plate. The inside seal cannot be as easily "blown" as the outside seal.

Secondary seals, often "o" ring-type but sometimes bellows, prevent leakage between housing and gland plate, primary ring and shaft, or mating ring and


Gland
Mating ring
Seal faces
Stuffing-box
Primary ring
Pumped liquid
Stuffing-box
Gland
Seal faces
Pumped liquid
Mating ring
Primary ring
Shaft

a. Outside seal

b. Inside seal

Figure E2-5. Single Mechanical Seals
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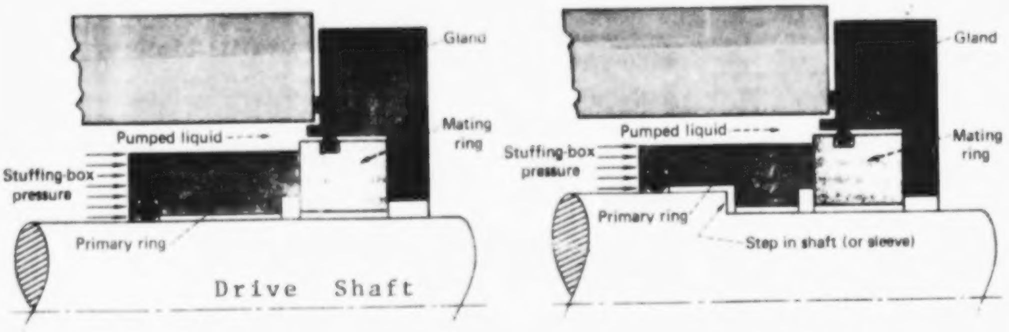
gland plate/stuffing box housing. The secondary seal must be sufficiently flexible so that the primary ring may move relative to the "sacrificial" mating ring when wear occurs or when one of the faces is not quite true. Typically, the primary ring is spring-loaded to maintain interfacial contact. Secondary seals are made of elastomers, plastics, glass-filled TFE or pure TFE. If the latter is used, a "v" or "u" shaped ring is necessary because of characteristic TFE cold-flow.[13] The properties of the secondary seal material are usually the limiting consideration in the application of mechanical seals. Figure E2-6 illustrates unbalanced and balanced inside seals. In the unbalanced seal, (a), the closing forces are the sum of the spring force (F_S) (spring not shown) and the force (F_{SB}) of the pumped liquid acting against the area of the left-hand side of the primary ring. Force F_{SB} is the product of the stuffing box pressure and the area of the primary ring perpendicular to the drive shaft, A_{DR}. The closing force, F_C, is opposed by the dynamic force, F_O, at the seal interface. Although leakage at the interface is small if the mechanical seal is installed and maintained correctly, an average pressure tending to force the lapped ring faces apart does exist, and its value lies between stuffing box pressure, P_{SB}, and ambient pressure, P_{AMB}. For calculations, the resulting average force is often taken to be linear and is therefore the product of the seal contact area, A_{SF}, and the average pressure at the face:


Gland
Mating ring
Pumped liquid
Stuffing-box pressure
Primary ring
Drive Shaft
Gland
Mating ring
Pumped liquid
Stuffing-box pressure
Primary ring
Step in shaft (or sleeve)

a. Unbalanced inside seal

b. Balanced inside seal

Figure E2-6. Balanced and Unbalanced Mechanical Seals

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$$F_O = A_{SF} \times \frac{(P_{SB} + P_{AMB})}{2}$$

Thus the net closing force, F_{NC}, is:

$$F_{NC} = F_C - F_O$$

$$= (F_S + F_{SB}) - F_O$$

$$= \left[F_S + (P_{SB} \times A_{DR})\right] - \left[\frac{(P_{SB} + P_{AMB})}{2} \times A_{SF}\right]$$

Because of the typically high wear rate associated with the unbalanced seal operating at high pressures, stuffing box pressures for this seal are limited to 25-100 psig, depending upon seal diameter and shaft speed.[13] By stepping or sleeving the drive shaft as shown in Figure E2-6(b), the hydraulic force F_{SB} acting on the exposed face of the primary ring can be reduced from that of an unbalanced seal. Differences in frictional forces favor the balanced seal by about 20 percent.[14]

Figure E2-7 is a more complete representation of a balanced internal seal. The spring-loading arrangement for the primary ring is shown. The seal coolant flow path shown allows liquid to pass over the mating rings. The liquid flushes any foreign matter toward the throat of the stuffing box and cools the rings near the contact surface. This type of flushing is not possible with the outside seal shown in Figure E2-5.

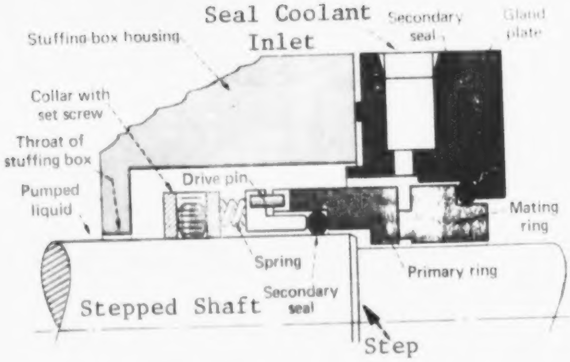
Seal Coolant Inlet
Stuffing box housing
Secondary seal
Gland plate
Collar with set screw
Throat of stuffing box
Drive pin
Pumped liquid
Mating ring
Spring
Primary ring
Secondary seal
Stepped Shaft
Step

Figure E2-7. Balanced Internal Seal Showing Seal Coolant Inlet.

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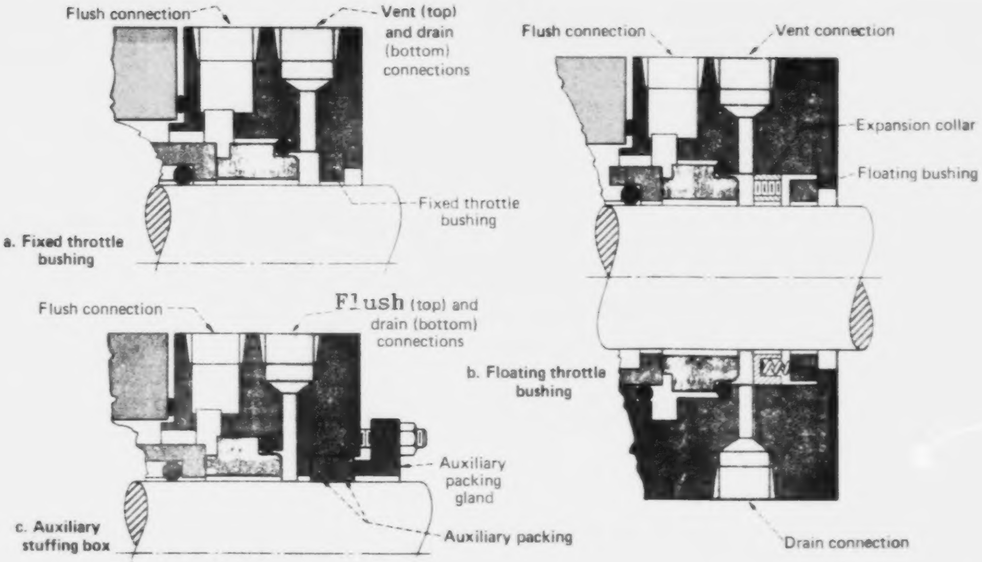
Thus liquid for a single inside seal is often the pump discharge liquid delivered via an auxiliary cooler and/or filter (if needed). If the pumped liquid flashes while passing across the seal faces or is otherwise a poor lubricant, a dissimilar but compatible liquid may be injected as coolant. Seal coolant is sometimes throttled at the throat of the stuffing box by positioning a lip seal or bushing there. Throttling reduces the loss of pump efficiency in the case of the recycle flush configuration; in all cases, a throttling device reduces the chance of debris entering the stuffing box from the pump casing.

A variation of the single mechanical seal involves placing a throttle bushing or auxiliary packing outboard of the single mechanical seal (Figure E2-8). The bushing or packing acts as a constriction to limit fluid escape in case of mechanical seal failure. The gland plate is drilled to provide vent and/or drain points for vapors and/or liquids which are flammable or toxic. Those fluids, should they escape, are ducted to appropriate disposal systems. If auxiliary packing [Figure E2-8(c)] is used as the back-up system, a water flush is introduced into the outboard flush connection. The water flush cools the packing as the water leaks out. The single mechanical seal/outboard restriction combination is less expensive than the double mechanical seals to be described next.


Flush connection
Vent (top) and drain (bottom) connections
Fixed throttle bushing
Flush connection
Flush (top) and drain (bottom) connections
Auxiliary packing gland
Auxiliary packing
Flush connection
Vent connection
Expansion collar
Floating bushing
Drain connection

a. Fixed throttle bushing

b. Floating throttle bushing

c. Auxiliary stuffing box

Figure E2-8. Back-up Systems for Seal Failure. Reprinted by special permission from CHEMICAL ENGINEERING[13]

Double Mechanical Seals - Double mechanical seals provide a margin of protection against seal failure not offered by single mechanical seals. Figure E2-9 illustrates one of two types of double mechanical seals, the "back-to-back" or "mirror image" arrangement.

Seal liquid pressure must be higher than stuffing box pressure in this configuration to prevent the inner primary ring from being blown back from the mating ring. Seal liquid normally lubricates both the inner and outer seal interfaces, passing into the stuffing box and also out past the outer seal faces and to the atmosphere from the seal housing. The seal liquid should, therefore, ideally be noncontaminating so that it will contaminate neither the pumped liquid nor the environment.

If the inner seal should fail, the outer seal would prevent escaping fluid from reaching the atmosphere. In case of accidental pressure loss in the seal liquid system, however, the pumped liquid would contaminate the seal liquid. If the seal liquid is contained within a pressurized "seal pot" system, the problem of contaminated seal liquid cleanup is minimized.

A second type of double mechanical seal is the tandem mechanical seal (Figure E2-10). In this form, the seals face the same direction, with the inner seal located inside the stuffing box housing rather than in the seal housing as in the "back-to-back" form.

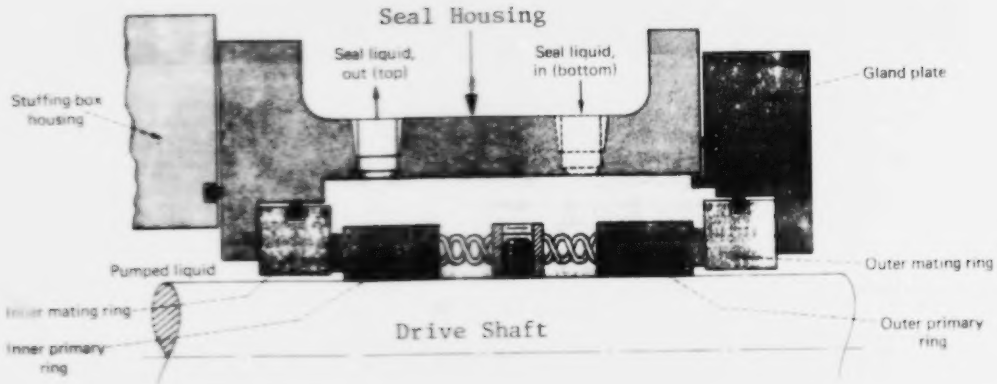

Seal Housing
Seal liquid, out (top)
Seal liquid, in (bottom)
Gland plate
Stuffing box housing
Pumped liquid
Outer mating ring
Inner mating ring
Inner primary ring
Drive Shaft
Outer primary ring

Figure E2-9. Double Mechanical Seal: Seal Liquid at Higher Pressure Than Pumped Liquid.

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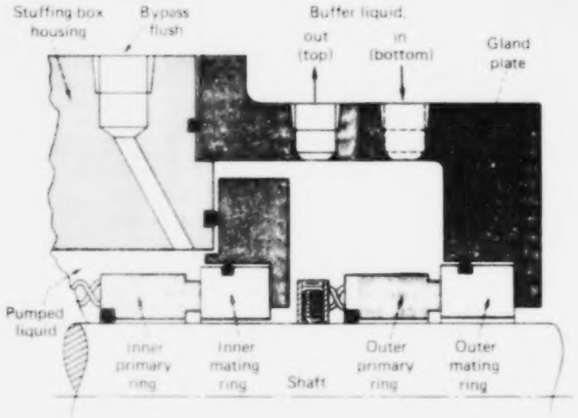
Stuffing-box housing
Bypass flush
Buffer liquid,
out (top)
in (bottom)
Gland plate
Pumped liquid
Inner primary ring
Inner mating ring
Shaft
Outer primary ring
Outer mating ring

Figure E2-10. Tandem Mechanical Seal: Buffer Liquid is at Lower Pressure than Pumped Liquid

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By contrast with the "back-to-back" double seal, which requires a seal liquid pressure higher than pumped liquid pressure, the tandem seal buffer liquid is at a lower pressure than the stuffing box pressure. This configuration protects the pumped liquid from buffer fluid contamination. This operational mode is possible because stuffing box pressure tends to close the seal faces, and loss of buffer pressure only increases the face seal pressure. In normal operation the buffer pressure is set so that it balances the opening/closing forces on the seal faces, minimizing both interfacial leakage and friction losses.

Should the inner seal of a tandem seal fail, pumped liquid would contaminate the barrier fluid, but would not be lost to the atmosphere except as it was lost slowly across the "back-up" outer seal face or by degassing through the reservoir vent. If a closed system is provided with pressure indicating/high pressure alarm devices as shown in Figure E2-11, very little time should be lost in taking action if inner seal failure should occur.[15]

Selected seal face materials are capable of service temperatures up to 750°F if coolant or flush liquid below 200°F is provided. Face combinations usually include a carbon/graphite mating ring because of the self-lubricating quality and softness of the graphite. Other ring materials include stellite, tungsten carbide, stainless steel, ceramics and Ni-Resist.[13]

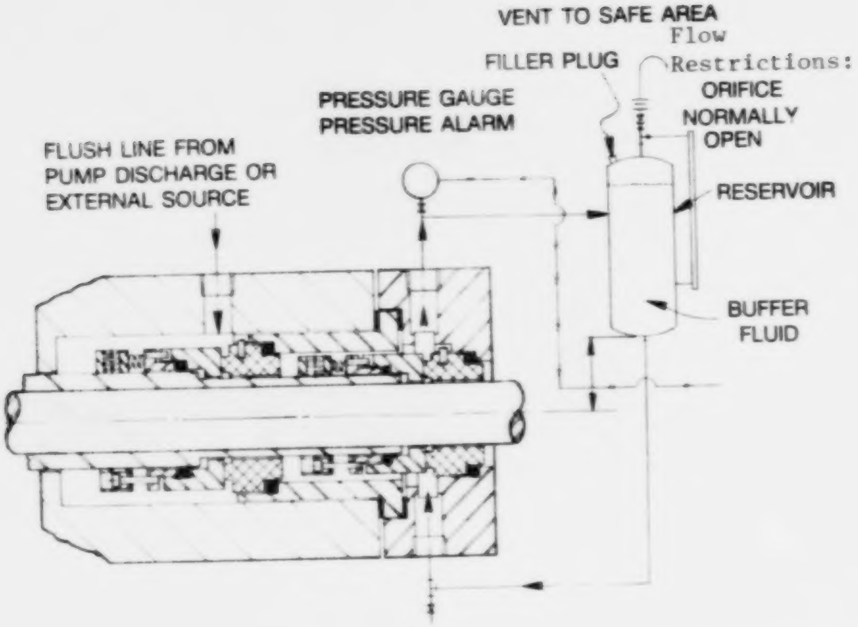

VENT TO SAFE AREA
Flow Restrictions:
FILLER PLUG
ORIFICE
NORMALLY OPEN
PRESSURE GAUGE
PRESSURE ALARM
FLUSH LINE FROM PUMP DISCHARGE OR EXTERNAL SOURCE
RESERVOIR
BUFFER FLUID

Figure E2-11. Tandem Seal with "Tell-Tale"
Pressure Gauge/Alarm

Reprinted by special permission from HYDROCARBON PROCESSING[15]

Guidelines and specifications for the application of packed and mechanical seals to centrifugal pumps in refinery service are found in API Standard 610.[16] Generally, recommendations cover:

- Minimum packing dimensions and number of packing rings,
- Location of coolant connections,
- Mechanical strength features of stuffing box,
- Requirements for water-smothering glands for pumps which handle high vapor pressure liquids,
- Seal back-up systems (auxiliary throttle bushings or packing),
- Piping for seals in clean service and for seals in dirty or special service.

Frequency of Application, Effectiveness, and Cost of Pump Seals--Application of the types of pump seals is relatively uniform within the refining industry. This may be the result of a greater uniformity of feedstocks and products in the refining industry than in the chemical industry. The application of standards published by the American Petroleum Institute (API) has also undoubtedly led to uniformity among devices used to control fugitive emissions, not only from pumps, but also from some of the other devices tested in this program.

The frequency of application of types of pump seals that was observed in the Radian sampling program is shown in Table E2-4. Emission factors for these seal categories were not statistically different (see Appendix B). This may be due to the use of mechanical seals in high volatility service. Sufficient data are not available for comparison of effectiveness of seal types for identical stream service.

TABLE E2-4. DISTRIBUTION OF PUMP SEALS IN RADIAN REFINERY STUDY

Pump Type	Percent of Population
A. Centrifugal Pump - Mechanical Seal	82.1
B. Centrifugal Pump - Packed Seal	11.5
C. Reciprocating Pump - Packed Seal	6.4
TOTAL	100.0

Table E2-5 is a cost breakdown of pump system elements for systems rated at 3-200 horsepower. May 1980 costs were rolled back to mid-1979. Cost estimates of packed and mechanical seals are shown in part (5) of the table in mid-1979 dollars, and in part (6) as percentage add-on costs to bare, uninstalled pump costs [Subtotal (4)]. These add-on costs for seals range from 1.2 to 3.0 percent for packed seals to 14.2 to 36.4 percent for double mechanical seals for the most common shaft size of 1.875 inches diameter.

Table E2-6 is a comparison of seal friction losses and hydrocarbon leak estimates for packed seals and three basic types of mechanical seals. Friction losses and hydrocarbon losses are known to vary widely with the fluid properties of the sealed

TABLE E2-5. CENTRIFUGAL PUMP SEALS - COST CONTRIBUTION TO TOTAL PUMP COST*

Pump Horsepower Shaft Diameter, Inches	3.0 1.875	100. 1.875	100. 2.375	200. 2.375
1. Pump, including shaft, coupling, bore plate, seal/bush hardware as required. (Installation costs not included)[a]	2830	4670	4810	6370
2. Switchgear - Switch, enclosure lighted push botton.[b]	620	1940	1940	4110
3. Driver - Electric[c]	230	2850	2850	8750
4. Subtotal	3680	9460	9600	19230
5. Seal Alternatives				
a. Packed Seal[d]	110	110	130	130
b. Single Mechanical Seal[e]	860	860	1000	1000
c. Double Mechanical Seal[f]	1340	1340	--	--
6. Seal Costs - Percentage of Subtotal (4)				
a. Packed Seal	3.0	1.2	1.4	0.68
b. Single Mechanical Seal	23.4	9.1	10.4	5.2
c. Double Mechanical Seal	36.4	14.2	--	--

*Mid-1979 Costs = May, 1980 Dollars x 0.921

Bases:

[a] Reference 17. Pump built to API Specification 610,[16] and upon the following conditions:
1) Low corrosion--steel pump casing, cast iron/steel impeller
2) Seal gland pressure--200 psig (~1/3 of discharge pressure maximum)
3) Pumped Fluid--light gasoline
4) Pumped Fluid Temperature-- $\leq$ 350°F
5) Shaft Speed--3500 RPM

[b] Reference 18. Switch gear--explosion-proof, locally-mounted push button stop-start with red light for "ON" indication.

[c] Reference 17. Electric Driver--Three phase, 400 volt, explosion proof.

[d] Reference 19. Packed Seal--Cost of packing materials approximate.

[e] Reference 20. Single Mechanical Seal--Crane Packing Co. #8-B-1 with throttle bushing as back-up.

[f] **Reference 19. Double Mechanical Seal--Chesterton Seal No. 241.**

TABLE E2-6. ESTIMATED ENERGY LOSSES - PUMP SEALS

Seal Type	Seal Power Consumption, kW[a]	Hydrocarbon Leak Estimates, lb/hr: Open Literature	Hydrocarbon Leak Estimates, lb/hr: This Study[b]
Packed	1.16	0.264[c]	
Single mechanical, unbalanced	0.422	≥0.0044[e]	0.16-0.37,[d] all pumps
Single mechanical, balanced	0.194	≥0.0044[e]	
Double mechanical, balanced	0.287	≅0.00[f]	

[a] Reference 14.

[b] See Appendix B, p. 2-263, pumps, light liquids.

[c] Based upon 60 drops/min of hexane @ 20 drops/mℓ. Reference 10.

[d] Range based upon 95% confidence interval.

[e] Based upon as little as 1 drop/min. of hexane @ 20 drops/mℓ. Reference 13.

[f] Reference 13.

Bases: Pump shaft dia.--1.875 in.; stuffing box pressure--200 psig; barrier fluid pressure--175 psig (double mechanical seal only); pump speed--3500 rpm; pump horsepower range (typical)--3-100 h.p.

liquid, the seal face materials, the condition of the seal, bearings and shaft, and seal design, so these figures are presented only as approximations of expected performance.

Inspection and Maintenance--All refineries practice inspection and maintenance of pump seals in order to prevent fire hazards resulting from complete seal failure. Pump seals are usually inspected visually once per day or per shift. Packed seals can be adjusted while in service to reduce leakage, but mechanical seals usually require removal for repair. The effectiveness of these inspection and maintenance programs is reflected in the emission factors presented in Appendix B.

2.2.3.2 Available Control Technology for Pumps

Leak detection and repair strategies are the available controls for pumps. The procedures for finding leaks requiring repair are the same as described for valves in Section 2.2.1.2. The hydrocarbon detector probe would be traversed around all potential leak areas, including barrier fluid degassing vents and the shaft seal junction. The probe should be prevented from contacting leaking liquids or the rotating shaft.

No data are available to quantify the effectiveness or cost of leak detection and repair for pumps. Effectiveness would be dependent on initial leak rates, the ability to repair the leaks, and the length of time before the leaks re-occurred. Costs would be dependent on labor rates, labor requirements, and the value of the product saved. Average leak detection time required for pumps has been estimated to be five minutes per seal, and the average leak repair time has been estimated to be 80 hours per seal.[8]

2.2.3.3 Technology Transfer for Pumps

Sealless pumps are used in other industries in cases where the pumped fluid is toxic or otherwise hazardous and leakage cannot be tolerated. Sealless pumps include diaphragm pumps, hermetically sealed "canned" pumps, and magnetically coupled pumps. Since these pumps do not have a shaft/casing seal, their emission potential is much lower. Emissions may result from diaphragm failure or case failure.

Sealless pumps are not covered by API Standard 610[16] from pumps, which may explain why no sealless pumps were found in the 13 refinery survey. If sealless pumps are to be used in the refining industry, they must be proven performers in terms of leak-tightness, reliability, maintainability, useful life and safety.

The original cost of a "canned" pump may be approximately 110 to 115 percent of the cost of a centrifugal pump with conventional seals.[21] No data are available to discern differences among the other true costs of running conventionally-sealed versus sealless pumps. Sealless pumps also have a more limited range of applicability due to limitations on temperature, throughput, and horsepower.

2.2.4 Compressors

Compressors can leak hydrocarbons at the junction of the shaft and body of the compressor or at the degassing reservoir of a seal oil system. Packed seals are the only type available for reciprocating shafts, and they are seldom used for rotating shafts. Rotating shafts can also be equipped with mechanical seals, labyrinth seals, restrictive ring seals, and liquid film seals. Thirty-seven percent of the compressors screened were in hydrogen service and 63 percent were in hydrocarbon service (Table B3-32, Appendix B).

2.2.4.1 Existing Controls for Compressors

The compressor seal and inspection and maintenance of the seal are the two types of existing controls for compressors.

Types of Compressor Seals--The American Petroleum Institute recognizes five basic types of seals which are applied to refinery compressors.[22,23] The frequency of application observed in the Radian study is shown in Table E2-7.

TABLE E2-7. TYPES OF COMPRESSOR SEALS

Shaft Type - Seal Type	Approximate Frequency of Observation, %
Reciprocating - Packed	67
Rotating - Labyrinth	5
Rotating - Restrictive Ring	0
Rotating - Liquid Film or Bushing	0
Rotating - Mechanical Contact (dry/wet)	10
Unidentified[a]	18
TOTAL	100

[a] Probably includes Restrictive Ring and Liquid Film seals

Source: Table B2-32, Appendix B.

Cooling of friction-type compressor seals differs from cooling of pump seals of similar construction in that the gaseous compressor working fluid provides negligible lubrication and has a lower heat capacity than does liquid. Therefore most, but not all, contact-type compressor seals use some form of liquid seal coolant which may also serve to reduce gas emissions.

Packed seals may be lubricated or non-lubricated. API Standard 618 suggests the increasingly higher cooling standards given in Table E2-8 for seal glands as discharge pressures increase.

TABLE E2-8. API RECOMMENDED COOLING STANDARDS

	Pressure Limits, psig	
Degree of Cooling	Lubricated Gland	Non-lubricated Gland*
Manufacturers Standard	≤ 1000	≤ 250
Indirect Cooling (Gland Jacket)	1000-1500	—
Direct Cooling through Packing Cup & Gland Jacket Cooling	≥ 1500	≥ 250

*Unlubricated packing assumed.

Source: Reference 11.

Also, according to API Standard 618, gases escaping the packing should be vented and piped from the "distance piece" separating the driver and compressor cylinder through an opening below the reciprocating rod.[11]

The labyrinth shaft seal is shown in its simplest form in Figure E2-11. A given gas at internal pressure escapes slowly to the atmosphere (or to an adjacent stage) at a rate which depends on shaft diameter, pressure differential, the closeness of fit of the labyrinth to the rotating shaft, and the number of "teeth" in the labyrinth.[24] In some designs, the edges score a sacrificial sleeve on the shaft to establish a tight fit and reduce leakage. As seen in Figure E2-12 a port may be provided which can be used for withdrawal of escaping gas (scavenging) or pressure purging inward and outward from the port. Nelson[24] states that the loss rate or recycle rate from this type operation is not generally acceptable today for energy and environmental reasons. For this reason, labyrinths are now more often seen in outboard seals in combination with other sealing devices, as seen in the illustrations to follow.

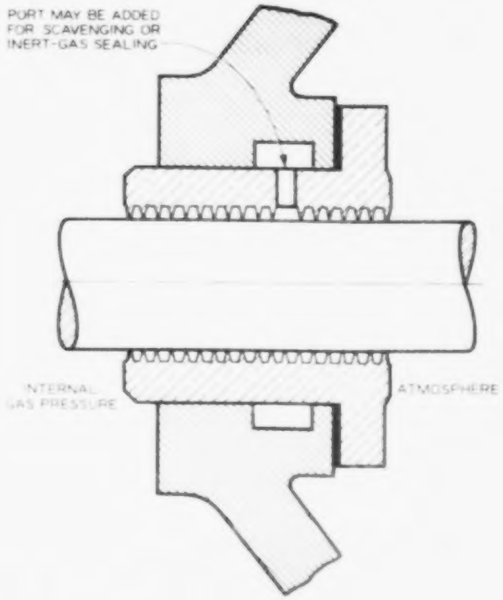

PORT MAY BE ADDED
FOR SCAVENGING OR
INERT-GAS SEALING
INTERNAL
GAS PRESSURE
ATMOSPHERE

Figure E2-12. Straight Pass Labyrinth
Compressor Shaft Seal.

Reprinted by courtesy of the American Petroleum Institute

Source: Reference 22, p.9.

A restrictive ring seal is illustrated in Figure E2-13. Fixed rings, often of carbon, are closely fitted without actually contacting the rotating shaft or shaft sleeve. The seal may be operated dry, with sealing liquid, or with a buffer gas. This type of seal is superior to the labyrinth seal alone, but is limited to about 200 psi and relatively clean gas service.[22,24] Sealing and scavenging ports may be used as for labyrinth seals.

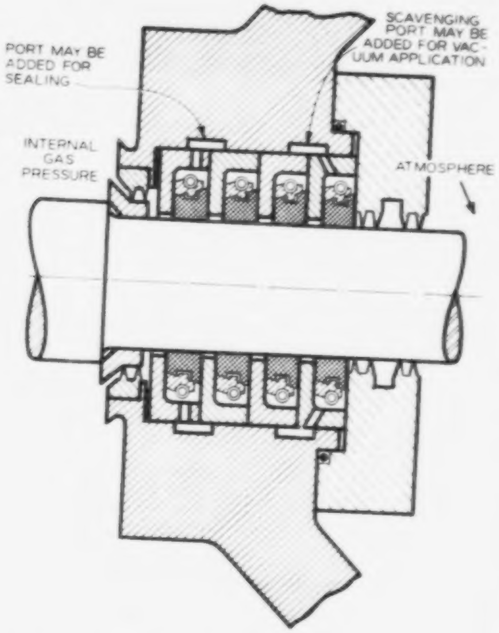

PORT MAY BE ADDED FOR SEALING
SCAVENGING PORT MAY BE ADDED FOR VACUUM APPLICATION
INTERNAL GAS PRESSURE
ATMOSPHERE

Figure E2-13. Restrictive-ring Compressor Shaft Seal.

Reprinted by courtesy of the American Petroleum Institute

Source: Reference 22, p.9.

Figure E2-14 depicts a liquid film, or bushing, seal. In this design, bushings are fitted within four to six thousandths of an inch of the shaft sleeve; they float with lateral shaft movement. Float is allowed by secondary elastomer seals on the outside of the bushings. Fresh sealant liquid entering the space between the inner and outer bushings flows both inward and outward. Inward flow is at a lower rate than outward flow because of the smaller available P driving force. If the gas being compressed is sour, the contaminated sealant oil must be treated. External piping and controls for surge, supply, recycle and makeup are diagrammed and described in API Standard 614.[25]

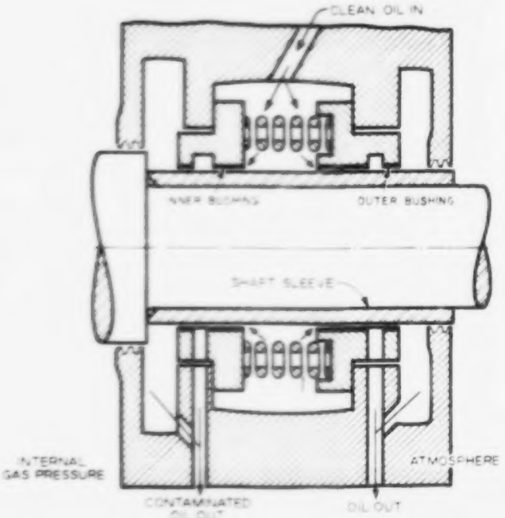

CLEAN OIL IN
INNER BUSHING
OUTER BUSHING
SHAFT SLEEVE
INTERNAL GAS PRESSURE
ATMOSPHERE
CONTAMINATED OIL OUT
OIL OUT

Figure E2-14. Liquid-film Compressor Shaft Seal with Cylindrical Bushing.

Reprinted by courtesy of American Petroleum Institute

Source: Reference 22, p. 10.

The liquid-film seal itself is relatively simple, and is not subject to significant wear. It is capable of operating at pressures of up to 5000 psi in a multiple seal configuration, but has, in all configurations, a relatively complicated piping and control system.[24]

The mechanical contact seal shown in Figure E2-15 differs significantly from a mechanical pump seal, but utilizes the identical concept of zero clearance at closely-lapped wear surfaces to limit leakage. The compressor seal has a floating carbon ring which rotates at about half compressor speed between a stationary and a rotating seat. The mechanical seal may be run "dry" (cooled and gas film lubricated by a seal gas), but interfacial pressures must be carefully regulated for "dry" operation.

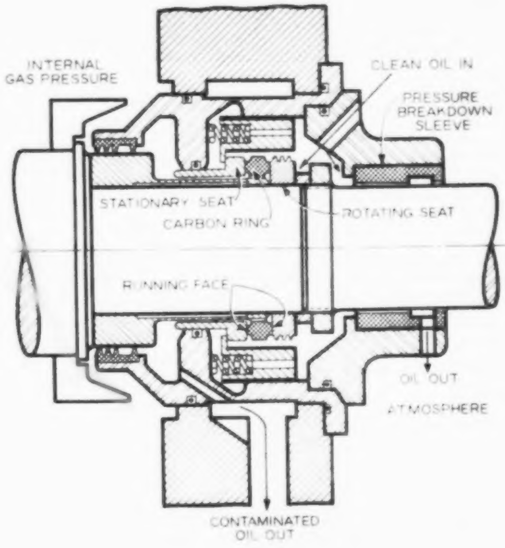

INTERNAL GAS PRESSURE
CLEAN OIL IN
PRESSURE BREAKDOWN SLEEVE
STATIONARY SEAT
CARBON RING
ROTATING SEAT
RUNNING FACE
OIL OUT
ATMOSPHERE
CONTAMINATED OIL OUT

Figure E2-15. Mechanical Contact Compressor Shaft Seal.
Reprinted by courtesy of American Petroleum Institute
Source: Reference 22, p.9

If the mechanical contact seal is liquid-lubricated, clean lubricant is introduced into the seal casing near the two friction surfaces of the carbon ring to aid heat-removal. The bulk of the oil is removed uncontaminated for recycle; a small portion passes the running faces and between the stationary seat and shaft, where it becomes contaminated and is withdrawn.

The mechanical contact seal is limited to pressures of $\leq$ 500 psi. Like mechanical seals for pumps, mechanical contact seals are subject to catastrophic failure. Their oil supply systems, where used, are simpler than oil supply systems for liquid-film seals.[24] Mechanical contact seals form a nearly perfect seal when at rest, which contrasts with pump mechanical seals that are believed to seal better when the faces are rotating.[24]

Effectiveness of Compressor Seals--Table E2-9 shows a comparison of seal leakage. The worst, the straight pass labyrinth, is given a gas leakage index of 100. It is not clear from the table, which includes both dry and lubricated seals, where the oil film seal fits in according to the gas leakage index. The liquid film seal is shown, however, to lose more lubricant than the lubricated mechanical contact seal by a factor of 55. It is not clear if this refers to oil loss into the compressed gas stream or if it refers to loss of oil (and dissolved gas) to the atmosphere.

The packed seal is the only seal available for a reciprocating compressor application. The mechanical contact seal, wet or dry depending upon design needs, would appear to rank the best among centrifugal compressor seals for pressures up to about 500 psi. However, these seals are said to be fragile and prone to failure, as well as complex and difficult to install correctly. It may be wise to limit applications to spare equipment or to investigate the history of a particular seal manufacturer's product before choosing this device.

TABLE E2-9. COMPRESSOR SEAL LEAKAGE

Compressor Seal	
Dry Types	Gas Leakage Index
Straight Pass Labyrinth	100
Staggered Labyrinth	56
Honeycomb Labyrinth	40
Restrictive Ring	20
Mechanical Contact (Running Dry)	2
Oil Types	Oil Loss
Mechanical Contact 6¾ in. Face Diameter 30 psi Differential 500 rpm	0.03 gal/hr
	Lubricant Loss
Liquid Film or Bushing 5½ in. Bore Diameter 0.007 in. Clearance 5000 rpm 60°F Oil Rise	1.75 gal/hr or 55 times the contact type

Source: Reference 24.

A more flexible device in terms of broad pressure range application (to 5000 psi) and suitability for dirty gas service is the liquid film seal. The complexity of its external circulation and control system would be perhaps its most costly feature.

Acid gas stripping from circulating seal oil is a must with the use of liquid film seals if the working gas is sour. The oil reservoir degassing vent may be a source of hydrocarbon emissions.

Seal Energy Requirements and Cost--Compressor seal design is traditionally an integral part of overall compressor design. As a result, data are not available to allow independent seal energy usage and cost analysis.

Inspection and Maintenance--Inspection and maintenance procedures for compressors are similar to those described for pumps. Leakage may be more difficult to detect because some compressors have enclosed seal areas that transport leakage to an elevated vent pipe. The effectiveness of these procedures is reflected in the emission factors for compressors shown in Appendix B.

2.2.4.2 Available Controls for Compressors

Closed vent systems and leak detection and repair programs are the available controls for compressors. A closed vent system consists of piping and, if necessary, flow inducing devices that transport compressor seal leakage to a control device. Control devices could include fired heaters or boilers, incinerators, flares, or vapor recovery systems. For compressors with seal oil systems, the closed vent system would be connected to the seal oil reservoir degassing unit. For other compressor seals, the seal area itself would be enclosed and connected to the closed vent system.

Leak detection and repair for compressors is similar to the program described for pumps. The hydrocarbon detector probe would be traversed around all potential leak areas. These areas would include the seal itself (if accessible), the seal vent pipe, and the seal oil reservoir vent depending on the physical configuration of the compressor. No data are available to quantify effectiveness of the leak detection and repair for compressors. Effectiveness and cost would be dependent on the same factors discussed for pumps. Average leak detection time required for compressors has been estimated as 10 minutes per seal, and repair time has been estimated as 40 hours per seal.[8] One major difference between repair of pump and compressor seals is that most refinery pumps have spares and most compressors do not. Therefore any repair that required compressor shutdown might also require shutdown of the process unit. Depending on the type of process unit, the unit shutdown could cause more emissions than allowing the compressor seal to leak until the next turnaround for repair.

2.2.4.3 Technology Transfer for Compressors

No other controls were identified for compressor seal leakage. Sealless compressors are not available in the range of throughput that would be required in almost any refinery application.

2.2.5 Agitators

Agitators may leak hydrocarbons at the junction of the vessel and the rotating agitator shaft. The agitator seal may be in liquid service if the agitator is located at the side of a storage tank, or the seal may be in vapor service if the agitator is located at the top of alkylation reactors. In some types of refinery operations, in-line blending has replaced the use of agitated mixing vessels.

2.2.5.1 Existing Controls for Agitators

The four basic types of agitator seals are shown in Figure E2-16. Some of the seals are similar to pump seals (packed and mechanical). The limitations of the four seal types are shown in Table E2-10. No data are available to establish the magnitude of leakage from agitator seals. The seals are listed in Table E2-10 in order of increasing cost.

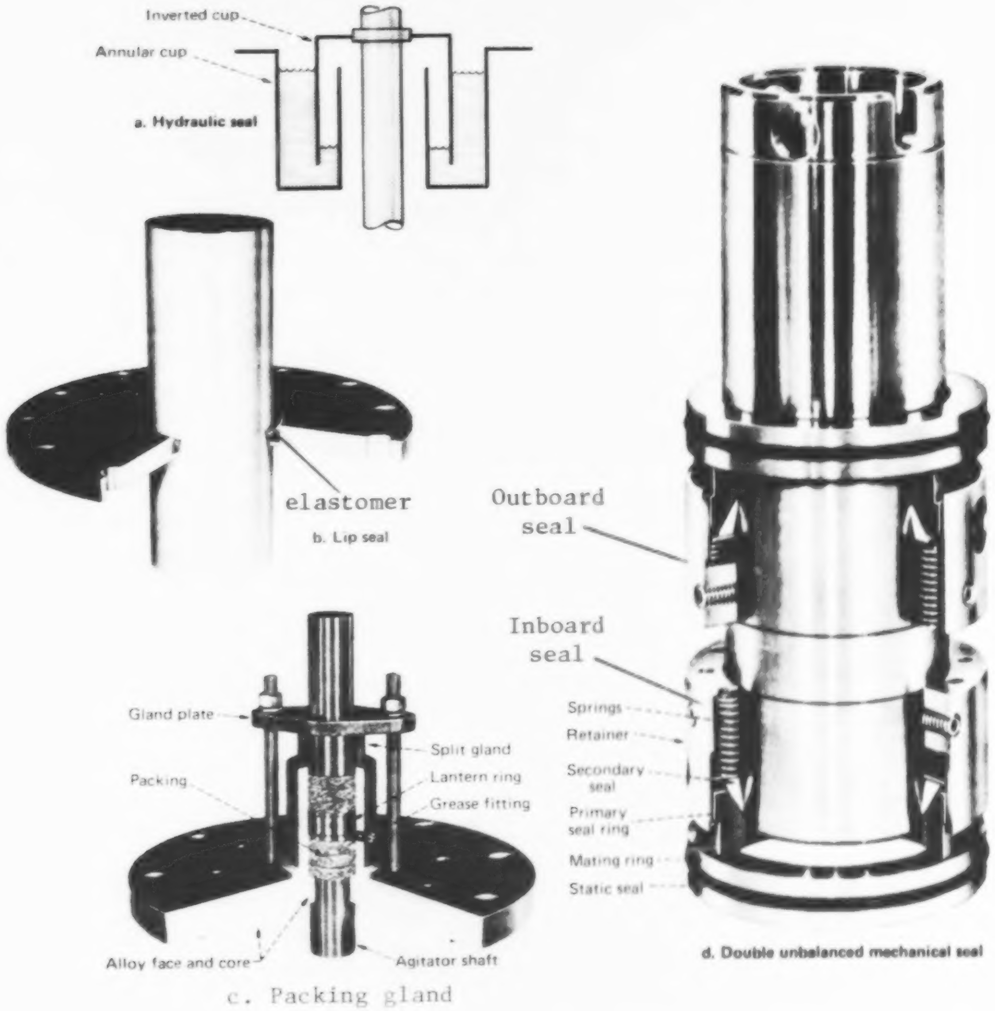
2.2.5.2 Available Controls for Agitators

Leak detection and repair strategies for agitators should be similar to those described for pumps and compressors. The time required to detect leaks is probably about the same as for pumps and compressors. The time requirements for repair are not quantified.

2.2.6 Pressure Relief Devices

Pressure relief devices are required in refining operations in order to protect process equipment from dangerous over-pressure conditions. The following terminology is used for valve-type pressure-relieving devices used in industry:[27]

- Relief Valve - primary liquid service,
- Safety Valve - for steam, gas and vapor services,
- Safety relief valve - for liquid or vapor services.


Inverted cup
Annular cup
elastomer
Gland plate
Packing
Split gland
Lantern ring
Grease fitting
Alloy face and core
Agitator shaft
Outboard seal
Inboard seal
Springs
Retainer
Secondary seal
Primary seal ring
Mating ring
Static seal

a. Hydraulic seal

b. Lip seal

c. Packing gland

d. Double unbalanced mechanical seal

Figure E2-16. Seals for Agitator Shafts.
Reprinted by special permission from CHEMICAL ENGINEERING[26]

TABLE E2-10. BASIC AGITATOR SEALS

Seal Type	Limitations	Comments
a. Hydraulic	Low pressure and temperature	Least-used agitator seal.
b. Lip	2-3 psi; unlubricated	Dust or vapor seal only; temperature limited by elastomer lip melting point.
c. Packing Gland	150 psi	Six packing rings and lantern ring required for 150 psi capability.
d. Mechanical Face	0 psia to 5,000 psia if housed and pressured to working fluid pressure	Externally lubricated so as to leak in if inboard seal fails (double seal configuration). Single seals also used.

Source: Reference 26.

In this appendix, the term "safety relief valve" (abbreviated SRV) will be used to designate all valves discussed. Fugitive emissions from SRV's may be the result of deterioration of the valve seat or incomplete closure of the valve seat after over-pressure release.

2.2.6.1 Existing Controls for Pressure Relief Devices

The three types of SRV's for use for hydrocarbon service are shown in Figure E2-17, and are described in Table E2-11. The type A SRV is probably the most common configuration found in refining. The Radian survey did not differentiate among SRV types.

TABLE E2-11. DESCRIPTION OF SRV TYPES

Type	Description	Application
A.	Standard spring-loaded angle-valve design, with top of relief disk at discharge-side pressure.	Discharge to atmosphere.
B.	Same as A above, except bellows isolate the bonnet so that top of disk is at atmospheric pressure when bonnet is vented to atmosphere.	Discharge to back-pressured header.
C.	Pilot operated SRV. Pilot valve opens at set pressure, relieving the pressure on top of main valve. Main valve then opens wide until blowdown pressure is reached, at which time the pilot valve closes, pressuring the top of the main valve by way of the supply tube pressure so that the main valve closes tightly.	Valve is capable of operating near the set pressure without "bubbling" or "simmering" type leaks.

a. Standard nozzle - guide vented to exhaust, bonnet plugged.

b. Balanced-bellows nozzle - bonnet vented to atmosphere.

c. Pilot-operated SRV.

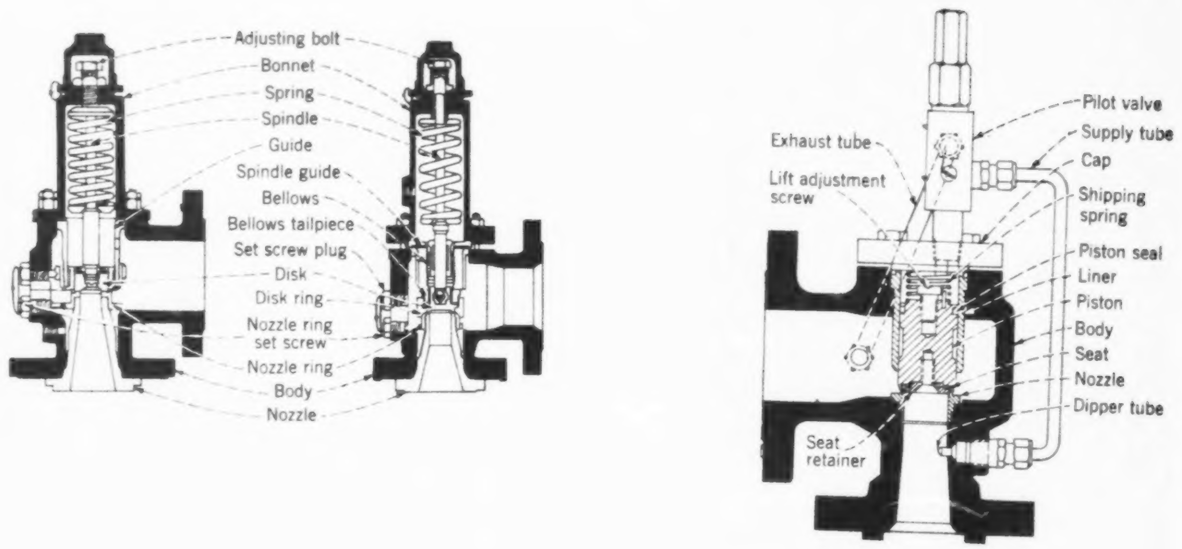

Adjusting bolt
Bonnet
Spring
Spindle
Guide
Spindle guide
Bellows
Bellows tailpiece
Set screw plug
Disk
Disk ring
Nozzle ring set screw
Nozzle ring
Body
Nozzle
Exhaust tube
Lift adjustment screw
Seat retainer
Pilot valve
Supply tube
Cap
Shipping spring
Piston seal
Liner
Piston
Body
Seat
Nozzle
Dipper tube

Figure E2-17. Typical Safety-Relief Valves.
Reprinted by special permission from CHEMICAL ENGINEERING[28]

Inspection and maintenance is one existing control for SRV's. The main objective of most inspection and maintenance programs is to make sure the SRV will provide proper over-pressure protection. Some companies remove and test SRV's after every overpressure release. This procedure requires that a means be provided to install a spare SRV while the other one is tested. Although this testing is primarily to check the set pressure of the SRV, it may also detect fugitive leakage. The other existing control for SRV's is discharge header systems that transport over-pressure releases (and fugitive leakage) to a flare.

E.2.4.2 Available Controls for Pressure Relief Devices

Leak detection and repair programs and upstream rupture disks are the available controls for SRV's. Leak detection would require periodic testing of SRV's that discharge to the atmosphere. The hydrocarbon detector probe would be placed at the exit of the discharge "horn" or at the weep hole at the bottom of the "horn". Repair of the SRV would probably require removal of the SRV, and therefore a means of replacing the SRV while the process unit was operating would be needed. Data on costs and effectiveness of leak detection and repair for SRV's are not available.

Although most SRV's are used alone or in pressure-stepped combinations, some are used with rupture disks mounted under them (i.e., between the process fluid and the SRV), as seen in Figures E2-18 and E2-19. Rupture disks (RD's) are somewhat prone to age-induced fatigue or corrosion failure, and therefore are not ordinarily used alone except where complete loss of process fluid is acceptable economically and environmentally. Such acceptable cases probably no longer exist in any organic chemicals or fuels manufacturing facility.

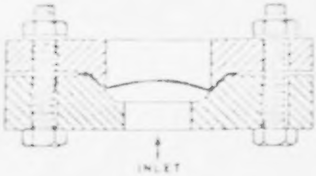


Figure E2-18. Rupture Disk and Hold-Down Flanges

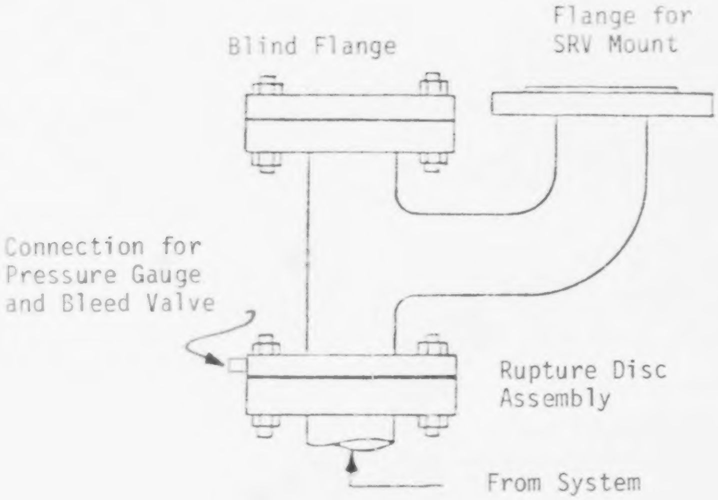

Blind Flange
Flange for SRV Mount
Connection for Pressure Gauge and Bleed Valve
Rupture Disc Assembly
From System

Figure E2-19. Relief Valve/Rupture Disk Assembly.

Rupture disks may be used upstream of SRV's as illustrated in Figure E2-19 to help prevent escape of refinery fluids provided means are established to monitor for small rupture disk leaks. Alternatively, they may be positioned downstream of SRV's to protect working parts from weather or other corrosive atmosphere, as when connected to a relief header.

Rupture disk leaks may be detected by "tell-tale" bubblers or pressure gauges, and by excess flow valves connected to the inside piping space between the RD and the SRV. This arrangement is covered by ASME code.[29] Such a pressure connection is shown in Figure E2-19 on the upper flange of the RD assembly. If small RD leaks are not monitored, there is a chance that the pressure between the RD and SRV might build to system pressure. Then, with a rapid rise in pressure, as in an emergency, working pressure would almost double before the disk and SRV would release, depending upon the rate of increase and size of the RD leak.

Effectiveness--As long as the integrity of the rupture disk is maintained, fugitive emissions are completely eliminated. The disk would require replacement after over-pressure release, and therefore a means for replacing it while the process unit was in service would be needed. Although there is controversy within the industry concerning the use of rupture disk-safety relief valve combinations, some feel that the combination may be operated safely.[29] Others consider RD use upstream or downstream of the SRV only as necessary for either 1) added isolation of particularly toxic materials from the air, or 2) as a means of isolating the SRV from a corrosive atmosphere. This atmosphere might be, for example, a header with sulfur compounds present, or simply salt air near the ocean.[28]

Costs--The addition of an inlet or outlet side rupture disk to an SRV adds between three percent and 50 percent to the materials cost of the SRV, depending on size and service. Materials costs for SRV and RD assemblies (excluding piping)are shown in Table E2-12. The net cost of the system would take into account a value for the product saved by eliminating fugitive emissions.

2.2.6.3 Technology Transfer for Pressure Relief Devices

Fugitive leakage caused by improper reseating after over-pressure release may be minimized by using pilot operated SRV's with resilient (O-ring) seats. No data are available to quantify the effectiveness of this type of control. Another potential improvement in SRV design would be to install parallel SRV's in all applications. This would allow an SRV to be in service, with the other blocked off as a spare. This would permit SRV removal for testing and rupture disk replacement after overpressure releases.

2.2.7 Sampling Connections

Fugitive emissions from sampling connections are the result of purging the sample line in order to obtain a representative sample. Atmospheric exposure of the purged fluid can result in evaporative hydrocarbon emissions.

2.2.7.1 Existing Controls for Sampling Connections

Existing practices for obtaining process samples vary considerably. They may range from draining process fluid onto the ground to collection of the purge in step oil systems. All

TABLE E2-12. SAFETY RELIEF VALVE (SRV) AND RUPTURE DISK (RD) ASSEMBLY COSTS

System Size, Inlet × Outlet diameter, inches	May, 1980 Dollars			
	SRV		RD Assembly	
	150 pri flanges	300 pri flanges	Inlet	Outlet
1 × 2	637	681	321	124
3 × 4	1,035	1,148	517	159
8 × 10	5,943	7,802	1,058	220[a]

Basis: Materials only; piping excluded. May, 1980 prices.
RD assembly includes cost of safety head and one disk.

---

[a] Interpolated from 4 inch and 12 inch diameter RD costs.

Source: Reference 30

existing practices result in some atmospheric exposure and emissions, but the magnitude has not been quantified.

2.2.7.2 Available Controls for Sampling Connections

Closed loop sampling systems are the primary control available to reduce sample purge emissions. A closed loop sampling system consists of a network of piping and valves that either returns the purged material directly to the process, or that transports the purge to a closed collection system for recycle.

2.2.7.3 Technology Transfer for Sampling Connections

The main innovations that are likely to reduce sample purge emissions are the increasing availability of on-line continuous analytical instruments that do not require discrete samples.

2.2.8 Wastewater Systems

Refinery wastewater systems include wastewater transport and wastewater treatment. Both operations can result in atmospheric exposure of hydrocarbon-containing streams and evaporative emissions.

Refinery wastewater treatment systems have evolved over the years as people have become aware of water pollution problems, and as various treatment systems have been developed. The basic treatment steps may be summarized as follows:[31]

- Primary Separation - The removal of oil by gravity separation. Normally, an API- or a CPI-type separator is used. These separators effectively remove free oil from water, but will not separate substances in solution nor break up emulsions.[32]

- Intermediate Separation - The removal of suspended solids and additional oil by chemical sedimentation or air flotation.

- Secondary Treatment - The reduction of the biological oxygen demand (BOD) with some type of biochemical oxidation.

- Tertiary Treatment - Removal of dissolved organics which will not degrade with biological treatment methods. Carbon adsorption is the most common form of tertiary treatment.

Classification of the numerous treatment processes into these categories is shown below.[33]

- Primary: API Separators
  Tilted-Plate Separators (CPI)
  Filtration for Oil Removal
  pH Control
  Stripping Processes

- Intermediate: Dissolved Air Flotation
  Coagulation-Precipitation
  Equalization

- Secondary-Tertiary: Carbon Adsorption
  Activated Sludge
  Aerated Lagoons
  Trickling Filters
  Waste Stabilization Ponds
  Cooling Tower Oxidation
  Chemical Oxidation
  Filtration

In addition, there is a wastewater collection system which consists of process drains, sewers, holding basins, and pumps. See Section 4.8.2.2 of Appendix F for a complete review of wastewater treatment systems.

Table E2-13 gives an estimate of the degree of adoption of various wastewater treatment processes for 1950, 1963, 1967, 1972, and 1977. While this table utilizes the author's judgement in many areas due to the "dearth of usable information," the data on API separators are reliable and confirm that by 1977 nearly all refineries had an oil and water separator of the API or the CPI type.[34]

Table E2-13 also shows an increasing use of intermediate secondary and tertiary treatment methods. This trend is a result in part, of Federal and state laws pertaining to water pollution. The Federal Water Pollution Control Act Amendments of 1972 established the need to install "best practicable control technology" by July 1, 1977 and to install "best available control technology economically achievable" by July 1, 1983.

A new set of Federal guidelines, developed in response to a successful legal challenge by environmental groups, requires that by 1984 industries must use "best available technology" to remove those compounds that have been deemed toxic to humans or

TABLE E2-13. DEGREE OF ADOPTION OF VARIOUS WASTEWATER TREATMENT PROCESSES

Processes and Subprocesses	% of Refineries Using the Process				
	1950	1963	1967	1972	1977
API Separators	40	50	60	70	80
Earthen Basin Separators	60	50	40	30	20
Evaporation	0-1	0-1	1	1-2	2-5
Air Flotation	0-1	10	15	18	20
Neutralization (Total Wastewater)	0-1	0-1	0-1	0-1	0-1
Chemical Coagulation and Precipitation	1-5	1-5	5-10	10-15	10-15
Activated Sludge	0	5	10	40	55
Aerated Lagoons	0	5	10	25	30
Trickling Filters	1-2	7	10	10	10
Oxidation Ponds	10	25	25	25	20
Activated Carbon	0	0.5	0.5	3	5
Ozonation	0	1	1	3	5
Ballast Water Treatment - Physical	9	9	8	5	5
Ballast Water Treatment - Chemical	1	1	2	5	5
Slop Oil - Vacuum Filtration	0	5	7	12	15
Slop Oil - Centrifugation	0	2	3	10	15
Slop Oil - Separation	100	93	90	80	70
Sour Water - Steam Stripping - Flue Gas Strippers - Natural Gas	60	70	85	90	90
Sour Water - Air Oxidation	0	3	3-5	7	10
Sour Water - Vaporization	1	1-2	1	0	0
Sour Water - Incineration[a]	35-40	40	50	30	20
Neutralization of Spent Caustics					
Flue Gas	20	30	35	20	20
Spent Acid (including springing and stripping)	15	25	30	25	20
Oxidation	0	3	5	5	5
Incineration	25	40	50	20	15

[a] Incineration includes flaring, boiler furnaces, and separate incinerators used only in conjunction with stripping and vaporization.

Source: Reference 34.

animals, or that are environmentally unacceptable. There are now 129 compounds that may eventually be subject to these specific removal guidelines.[35]

The relationship between wastewater flowrate and crude oil throughput has been shown to vary widely among refineries. Newer or updated refineries do a better job of segregating process water from storm water. Wastewater flow rates may range from six barrels per barrel of crude in old refineries to as little as 0.8 barrels per barrel of crude in new refineries.[37] Table E2-14 shows typical removal efficiencies for the various refinery wastewater treatment processes.

Higher water/oil ratios require more oil and water separator surface area and thus increase the fugitive emissions from the separators. The required surface area is a function of the wastewater flow rate, the oil density, and the oil content of the effluent water. In designing an API separator, the total surface area is obtained from these three factors, then the configuration of the separator is determined by using the following guidelines:[38]

- Velocity should not exceed two feet per minute.
- Length-to-width ratio should be at least five to avoid dead spots in the separator.
- Minimum depth should be four feet.

2.2.8.1 Existing Levels of Control for Wastewater Systems

Current Emissions--The problem of determining and controlling fugitive emissions to the atmosphere from refinery wastewater systems is clouded by several factors. First,

TABLE E2-14. TYPICAL REMOVAL EFFICIENCIES FOR OIL REFINERY TREATMENT PROCESSES

Process Number	Process	Process Number of Process Influent	Removal Efficiency, %							
			BOD_5	COD	TOC	SS	Oil	Phenol	Ammonia	Sulfide
1	API Separator	Raw Waste	5-40	5-30	NA	10-50	60-99	0-50	NA	NA
2	Clarifier	1	30-60	20-50	NA	50-80	60-95	0-50	NA	NA
3	Dissolved Air Flotation	1	20-70	10-60	NA	50-85	70-85	10-75	NA	NA
4	Filter	1	40-70	20-55	NA	75-95	65-90	5-20	NA	NA
5	Oxidation Pond	1	40-95	30-65	60	20-70	50-90	60-99	0-15	70-100
6	Aerated Lagoon	2,3,4	75-95	60-85	NA	40-65	70-90	90-99	10-45	95-100
7	Activated Sludge	2,3,4	80-99	50-95	40-90	60-85	80-99	95-99+	33-99	97-100
8	Trickling Filter	1	60-85	30-70	NA	60-85	50-80	70-98	15-90	70-100
9	Cooling Tower	2,3,4	50-90	40-90	10-70	50-85	60-75	75-99+	60-95	NA
10	Activated Carbon	2,3,4	70-95	70-90	50-80	60-90	75-95	90-100	7-33	NA
11	Filter Granular Media	5-9	NA	NA	50-65	75-95	65-95	5-20	NA	NA
12	Activated Carbon	5-9 plus 11	91-98	86-94	50-80	60-90	70-95	90-99	33-87	NA

NA = Data not available.

Source: Reference 36.

wastewater systems are designed to treat wastewater and it is that function which receives the most attention. Second, refinery wastewater systems vary tremendously as to volumes of process water, storm water, particulates, oil and grease, and other contaminants. Third, refinery wastewater systems vary from one refinery to the next. The only common denominator is an oil and water separator of the API or CPI type, although the actual configuration of these separators may vary considerably. Fourth, reliable test data on hydrocarbon emissions from refinery wastewater systems are not available.

Most sources give emission figures which stem from the estimates made for the Los Angeles area in 1958. In that early study, hydrocarbon emissions from wastewater separators from existing refineries in the Los Angeles County area were estimated to range from 10 lb/1000 bbls refinery capacity to 200 lb/1000 bbls refinery capacity.[39] Supplement 8 of AP-42 (May, 1978) lists the hydrocarbon emission factors shown in Table E2-15. These emission factors are for the combined emissions of drains and wastewater separators.

TABLE E2-15. WASTEWATER SYSTEM EMISSION FACTORS

Control	Emission Factor ($lb/10^3$ bbl refinery feed)
Uncontrolled	200
Vapor recovery; separator covers	10

The results of Radian's oil/water separator emission sampling are shown in Appendix B, Tables B3-12 through B3-20. The results are not shown here because it appears that some of the data are invalid due to difficulties in obtaining representative samples and in applying the test methods used. The emission factor for process drains is shown in Table B2-23. The mean value is 0.07 pounds of hydrocarbon per hour for each drain. The 95 percent confidence intervals for the mean estimate are (0.023, 0.20).

Current Controls--Covered oil/water separators and trapped drain systems are two types of emission controls used in some refineries. Some state regulations require covers for separators, and as of January 1977, 80 percent of the U.S. refining capacity was located in states where covers are required.[41] The extent of application of trapped drain systems is not known. Because of the lack of emission data, effectiveness of those controls cannot be assessed. Costs would vary, depending on site specific conditions.

The current AP-42 emission factors for drains and oil/water separators, uncovered versus covered, imply a 96 percent fugitive hydrocarbon emission reduction. The original reference upon which the AP - 42 emissions are based is, according to the California Air Resources Board (CARB) no longer available.[42] In a laboratory study using a simulated API separator, the covered separator provided 89 percent emission reduction.[43]

2.2.8.2 Available Controls for Wastewater Systems

In general, available controls for reducing fugitive emissions from existing process and storm sewers and collection systems consist of relatively minor modifications such as sealing open sewer systems, altering pump bases, recurbing some process areas, and improving housekeeping practices.

Changes which involve substantial capital outlays (or which may be infeasible from a construction standpoint) such as major revisions to existing underground sewer systems or installation of vapor recovery systems probably do not represent best available technology economically achievable. Techniques which are considered reasonable controls for emissions from the collection system are listed below.

- Open drains, sewers, or holding basins upstream of the oil and water separator: these sources of emissions in the U.S. refining industry are now fairly rare. The evaporation of significant volumes of oil at current world scale prices is a readily apparent financial burden. Obviously, holding basins should be eliminated and process drains and sewers sealed or vented through liquid seals.

- Pump bases which do not drain completely by gravity: many pump bases are designed so that a slight level of oil (from a leaking seal) must build up before the base drains to the sewer. When new pumps are to be installed, bases should be selected which allow proper drainage. Existing pump bases can be modified at minor cost.

- Segregation of process water from storm water: oily water volumes should be minimized. Curbing should be installed so that only those areas which are subject to oil spills drain into the oily water sewer system. Storm sewers should be sized so that overflow into process sewers during peak runoff is avoided. In many cases, however, substantial revisions to the sewer systems of older plants will be prohibitively expensive.

- General housekeeping: an undefined but in some cases significant source of emissions is the lack of good housekeeping practices concerning oil spills and leaks. A quantitative control technique in the area of oil spills and leaks could probably not be formulated, but an awareness of the problem would be beneficial.

2.2.9 Cooling Towers

Cooling towers can emit hydrocarbons that contaminate the circulating cooling water. The hydrocarbons may enter the cooling water as a result of leaks in heat exchangers or as a result of using contaminated process water as cooling tower make-up water. When the contaminated water is cascaded through the cooling tower, hydrocarbons can be evaporated and emitted to the atmosphere.

2.2.9.1 Existing Control Levels for Cooling Towers

At the time of the 1958 Los Angeles County California Emissions Study,[44] "atmospheric sections" (splash-cooled heat exchanger tubes) could still be found in refinery cooling towers, although they were prone to leak and were difficult to repair. Chromates and chlorine were used to control corrosion and biological growth, respectively. The emission factor for cooling towers was estimated to be 6.2 lb hydrocarbons/10^6 gal cooling water circulation.

By 1978, wetted "atmospheric" sections had generally been phased out of refineries. Organo-phosphates had replaced chromates for corrosion control; biological growth was being controlled by combinations of chlorine and, often, nonoxidizing biocides.

Today, as in 1958, make-up water ranges from near-pristine snow-based surface water to sea water. Some refineries now recycle water from sour water strippers, which tends to reduce total plant water effluent and retain phenols in the plant. During recycling in a cooling tower, the aeration encourages oxidation of phenols in the stripper bottoms water.

Emission factors determined during this study were based on two analytical methods: Total Organic Carbon (TOC) Analysis and a purge technique (see Appendix A). These results bracket the 1958 emission factor of 6.2 $lb/10^6$ gal cooling water, as shown in Table E2-16.

TABLE E2-16. RADIAN-GENERATED COOLING TOWER EMISSION FACTORS

Analytical Technique	Emission Factor $lb\ HC/10^6$ gal C.W. (Appendix B)
TOC	12.4
Purge	0.108

Because of variations in sampling and analytical techniques, these results are inconclusive. There is also a wide variation in the quality of water that is used as cooling tower make-up, and therefore large differences may be expected at different facilities.

2.2.9.2 Available Controls for Cooling Towers

The best control for cooling towers is to minimize the amount of hydrocarbons entering the tower. One method to achieve this goal is to eliminate the use of contaminated process water as cooling tower make-up. This may be difficult, since efforts to reduce water discharges may require the use of process water for cooling towers. Another control option is to monitor the hydrocarbon content of the cooling tower input. If elevated concentrations were detected, a leak in the process equipment would be indicated. The problem then is to identify the specific leak and to repair it. Ambient air monitors could also be used to measure the hydrocarbon concentration in the cooling tower plume. Because of variable meteorological conditions, this method would be difficult to apply.

2.2.10 Solid Waste System Alternatives

Petroleum refineries generate numerous solid waste streams, which may contain many substances. These streams may be divided into two main groups: intermittent and continuous. Typical intermittent waste streams are as follows:[36]

- process vessel sludges, vessel scale and piping deposits,
- storage tank sediments,
- produce treatment wastes, such as filter clay and spent catalysts from certain processing units.

Typical continuous waste streams are as follows:[36]

- coke fines from cokers and spilled coke from unloading facilities,
- fluid catalytic cracker catalyst,
- spent and spilled grease and wax from lube oil processing plants,
- waste biological sludges from activated sludge units,
- floating solids from dissolved air flotation unit.

Most solid wastes are residuals from wastewater treatment. The exceptions to this are some spent catalysts which are recovered in segregated containers, spent acids and caustic, and other spills and sediments which can be segregated. Normally these exceptions are handled separately from other solid wastes.

Fugitive emissions from solid waste disposal could be particulate matter or evaporative emissions of residual hydrocarbons. The only control option available is to minimize the amount of atmospheric contact of the wastes during handling and disposal. Therefore, the following sections only describe the types and amounts of solid wastes produced in refineries, and the waste disposal practices used.

2.2.10.1 Existing Solid Waste Disposal Practices

The five general categories of solid waste disposal alternatives are listed below.[45] The first three of these disposal alternatives can create emissions to the atmosphere.

- Landfarming
- Incineration (with landfilling of the ash)
- Landfilling
- Deep-well injection
- Solidification (producing relatively inert substances which chemically or physically isolate the pollutant, or surrounding the pollutant by encapsulation)

Landfarming, incineration, and landfilling are the most common methods of disposal for refinery solid wastes. A 1976 summary of solid waste disposal practices by Jacobs Engineering Company describes disposal practices of the U. S. refining industry.[46] Unless otherwise noted, percentages of adoption figures are for the year 1973.

Crude Tank Bottoms--Crude tank bottoms are oil-water emulsions containing large quantities of solids and colloidal material which have settled to the bottom of the tank. In general crude tank bottoms are not flammable at ambient conditions, but can be hazardous due to their heavy metals and oil content. About 14 percent of the U. S. refineries are known to be landfilling these wastes, 23 percent are landfarming, 6 percent are landfilling in a "secure" site (California Classification Class 1), and less than 1 percent are landfarming on a "secure" site. Practices at the remaining refineries are not known.

Straight landfilling is an inadequate method of disposal due to the danger of migration of oil and/or heavy metals from the site. Landfarming appears promising, but more information is needed about best operating methods and degradation products.

Leaded Gasoline Sludges--Sludge from leaded gasoline storage tanks contains precipitated organic lead compounds in a mixture of gasoline, other additives and tank scale. The typical organic lead concentration in fresh sludge is 100 to 200 ppm. This sludge produces organic lead vapors which are toxic at very low concentration (OSHA limits are 0.075 to 0.15 mg/m^3). Other hazardous constituents are phenols, arsenic, selenium, mercury, cobalt, nickel, zinc, cadmium, and molybdenum.

About 61 percent of U.S. refineries pump leaded gasoline tank bottoms into an excavated pit, allow it to evaporate and weather for one to four months, and then cover the pit. The disposal method is often inadequate since dangerous organic lead concentrations remain years after covering. An alternative procedure used by 39 percent of U. S. refineries is to spread the sludge two to four inches thick on a curbed concrete pad and allow it to weather until the organic lead concentration is below 20 ppm. The residue is then placed in a sanitary landfill.

Non-leaded Tank Bottoms--Non-leaded tank bottoms sludge waste is generated when tank sediment levels become too high (once every one to five years) or when tank service is changed (which occurs annually for many tanks such as diesel/gasoline switch tanks). This sludge is put in an approved sanitary landfill in 57 percent of U. S. refineries. This disposal technique merely allows the petroleum to be adsorbed into the soil and stored until it leaches out or is degraded. About 23 percent of the refineries landfarm this sludge. This method is promising.

API Separator Sludge--API separator sludge is a heavy black oily mud which contains relatively high concentrations of phenols, Cr, Se, Hg, Co, Cu, Zn, Cd, Pb and Mo. In 1973 about 53 percent of U. S. refineries landfilled API separator sludge in unsecured sites, while another seven percent landfilled in secured sites. Landfilling in an unsecured site will not be acceptable by future standards. In 1976, seven percent of these sludges were being landfarmed.[47] By 1979 about half of these wastes were being landfarmed.[48]

Hydrofluoric Acid Alkylation Sludge--A cream-brown slurry of insoluble CaF_2 sludge is produced when HF acid is neutralized with spent lime. While HF is extremely hazardous, when it has been properly neutralized with lime the resultant precipitate can be landfilled without much risk to ground waters. Landfilling is the normal disposal technique.

Kerosene Filter Clays--Kerosene filter clays contain oil and heavy metals. These sludges are landfilled in secure or unsecure sites. Danger of leakage from unsecured landfill is high. Landfarming is an option.

Once-Through Cooling Water Sludges--Silt from the raw water supply, process leakage, and corrosion products are settled in clarification basins. The silt or mud has occluded oil and heavy metals such as As, Hg, Mo, Pb and Se. These basins are periodically drained and dredged and the silt landfilled or landfarmed in secured or unsecured sites. Unsecured sites present groundwater contamination hazards in landfill disposal.

Dissolved Air Flotation (DAF) Float--DAF float contains oil and heavy metals. It is normally trucked to a landfill or a landfarm site. Once again, unsecured landfill sites may be hazardous to groundwaters.

Slop Oil Emulsion Solids--Crude and other petroleum fractions recovered from spills and interception points within the refinery are often too contaminated to be rerun in the plant. These wastes can be landfarmed or landfilled in secure or unsecure sites. Potential exists for quantity reduction through centrifugation or filtration.

Spent Lime from Boiler Feedwater Treatment--The spent lime slurry from boiler feedwater softeners contains mixtures of calcium, magnesium and other carbonates; hydroxides; silt; organic matter and water. The metals are effectively tied up in the sludge and minimal hazard is present.

Cooling Tower Sludge--Cooling tower sludge contains high concentrations of several heavy metals, particularly hexavalent chromium and zinc. In addition, copper, lead, arsenic and selenium are present in relatively high concentrations.

In 1973, 81 percent of U. S. refineries trucked this sludge to unsecured landfill sites while only eight percent were known to landfill in secured sites. Unsecured site landfilling presents possible danger to groundwaters.

Exchanger Bundle Cleaning Sludge--Exchanger bundle cleaning creates a residue of metal scale, coke, particulate matter, and oil. These wastes are landfilled in secure or unsecure sites. The oil and heavy metals content of the material makes unsecure landfilling potentially hazardous to groundwaters.

Waste Bio Sludge--The organic cell material synthesized by microorganisms during secondary wastewater treatment is periodically wasted to maintain steady state conditions. This material is landfilled in secured sites (19 percent of U. S. refineries in 1973), landfarmed (25 percent) or landfilled in unsecure sites (15 percent). Landfarming this waste is becoming more frequent as techniques are improved.

Storm Water Silt--Storm water runoff picks up soil, oil, spilled solutions, metals, coke fines and other miscellaneous substances. Twenty-four percent of U. S. plants were known to landfill this material in unsecured sites in 1973, four percent landfilled in secure sites. Secured sites are needed for adequate disposal.

FCC Catalyst Fines--FCC catalyst fines consist of a fine grey powder of aluminum silicate with absorbed heavy metals, primarily vanadium and nickel. During transfer operations, the dust may become airborne, so workers should wear goggles and filtering masks. In 1973, 30 percent of the refineries were known to be transporting these fines to unsecured landfill sites and eight percent were known to use secured sites. Unsecured sites are subject to leaching of heavy metals into groundwaters. Many refineries contract for removal of this waste by companies which specialize in handling this material. Several companies are investigating the feasibility of using FCC fines as alumina cement additive and of recovering aluminum and vanadium.

Coke Fines--Grey-black chunks and particle fines from coking units are generated by spillage during transport and loading of coke, by contamination of coke with earth during stockpiling, and by mixing with water during removal from the drum.

Most refineries landfill this waste. High concentrations of vanadium and nickel make a secured landfill the preferred disposal technique.

2.2.10.2 Amount of Wastes Produced

Table E2-17 gives the total estimated solid waste generation rate for U. S. refineries. Boiler feedwater lime sludge accounts for over 60 percent of the tonnage of waste in this 1975 survey. This source is not a major problem since the sludge is not hazardous, and since lime treating of boiler feedwater is gradually being replaced with demineralization processes.

TABLE E2-17. TOTAL ESTIMATED U. S. REFINERY SOLID WASTE GENERATION RATE

Solid Waste Stream	Total Tons/yr	$lb/10^3$ BBL Crude
Crude Tank Bottoms	830	0.3
Leaded Gasoline Sludge	1,840	0.7
Non-Leaded Tank Bottoms	91,500	35.8
API Separator Sludge	76,500	29.9
HF Acid Alkylation Sludge	18,430	7.2
Kerosene Filter Clays	4,800	1.9
Once-Through Tooling Water Sludge	41,300	16.2
Dissolved Air Flotation Float	66,200	25.9
Slop Oil Emulsion Solids	37,200	14.6
Boiler Feedwater Lime Sludge	858,700	336.1
Cooling Tower Sludge	500	0.2
Exchanger Bundle Cleaning Sludge	1,450	0.6
Waste Bio Sludge	89,500	35.0
Storm Water Silt	33,200	13.0
FCC Catalyst Fines	34,100	13.3
Coke Fines	3,820	1.5
TOTAL	1,359,870	532.2

Note: Unit loads are based on a total U.S. refinery capacity of $14x10^6$ BPD.

Source: Reference 45.

2.3 References

1. Pikulik, A. Selecting and Specifying Valves for New Plants. Chem. Eng., 83(19):168, 1976.

2. Scott, Carleton B. Union Oil Company of California. Letter to Don R. Goodwin, EPA:ESED, December 3, 1976, response to EPA request for information on miscellaneous hydrocarbon emission sources from refineries.

3. Van Ingen, R. E. Shell Oil Company. Letter to Don R. Goodwin, EPA:ESED, January 10, 1977, response to EPA request for information on miscellaneous hydrocarbon emission sources from refineries.

4. Amey, Guy C., Century Systems Corporation. Letter to Jim Serne, Pacific Environmental Services, Inc., October 17, 1979.

5. Johnson, J. M., Exxon Company, Letter to Robert T. Walsh, EPA:CPB, July 28, 1977, comments on 1st draft report, "Control of Hydrocarbons from Miscellaneous Refinery Sources."

6. Pikulik, A. Manually Operated Valves. Chem. Eng., 85(8): 119, 1978.

7. Perry, R. H. and C. H. Chilton. Chemical Engineers Handbook, 5th edition. McGraw-Hill, New York, New York, 1973.

8. California, State of, Air Resources Board, Legal Affairs and Enforcement of Stationary Source Control Divisions. Emissions from Leaking Valves, Flanges, Pump and Compressor Seals, and Other Equipment at Oil Refineries. Report No. LE-78-001, Sacramento, California. April 1978. Page I-2.

9. Frazier, William, Crane Co., Houston, Texas. Telephone conversation with W. R. Phillips, Radian Corporation, Austin, Texas, June 18, 1979.

10. Hoyle, R. How to Select and Use Mechanical Packing. Chem. Eng., 85(22):103, 1978.

11. American Petroleum Institute, Division of Refining. Manual on Disposal of Refining Wastes, Volume on Atmospheric Emissions. API Pub. No. 931, Washington, D.C., 1976.

12. Steigerwald, B. J. Emission of Hydrocarbons to the Atmosphere from Seals on PUmps and Compressors. Report No. 6. Joint District, Federal and State Project for the Evaluation of Refinery Emissions and Los Angeles County Air Pollution Control District, Los Angeles, California, April 1958.

13. Ramsden, J. H. How to Choose and Install Mechanical Seals. Chem. Eng., 85(22):102, 1978.

14. Center for Professional Advancement. Mechanical Seal Technology for the Process Industries. East Brunswick, New Jersey, March 1978.

15. Block, H. P. Improve Safety and Reliability of Pumps and Drivers, Part 4. Hydrocarbon Processing, 56(4):181, 1977.

16. American Petroleum Institute, Refining Dept. Centrifugal Pumps for General Refining Services, 5th edition. API Standard 610. Washington, D.C., March 1971.

17. Richards, C. J. Pacific Pump Division of Dresser Industries, Houston, Texas. Private communication with W. R. Phillips, Radian Corporation, Austin, Texas, May 15, 1980, regarding Pump and Driver costs for 3 - 100 h.p. pumps with 1.875 - 2.375 in. dia. shafts.

18. Voden, James, Allen-Bradley Co., Houston, Texas. Private communication with W. R. Phillips, Radian Corporation, Austin, Texas, May 15, 1980, regarding electric switchgear for pump motors.

19. Adams, C. S., Gulf Coast Packing and Seal Co., Inc., Houston, Texas. Private communication with W. R. Phillips, Radian Corporation, Austin, Texas, May 1980, regarding A. W. Chesterton pump seals and packings.

20. Fadner, D. D., Crane Packing Co., Houston, Texas. Private communication with W. R. Phillips, Radian Corporation, Austin, Texas, May 1980, regarding costs and applications of John Crane Mechanical Seals.

21. Potter, Charles, Crane-Deming Pump Co., Houston, Texas. Telephone conversation with W. R. Phillips, Radian Corporation, Austin, Texas, September 27, 1979.

22. American Petroleum Institute, Refining Dept. Centrifugal Compressors for General Refinery Sources, 3rd edition. API Standard 618. Washington, D.C., October 1973.

23. American Petroleum Institute, Refining Dept. Reciprocating Compressors for General Refinery Service, 2nd edition. API Standard 618. Washington, D.C., July 1974.

24. Nelson, W. E. Compressor Seal Fundamentals. Hydrocarbon Processing, 56(12):91, 1977.

25. American Petroleum Institute, Refining Dept. Lubrication, Shaft-Sealing, and Control Oil Systems for Special Purpose Applications. API Standard 614. Washington, D.C., September 1973.

26. Ramsey, W. D. and G. C. Zoller. How the Design of Shafts, Seals and Impellors Affects Agitator Performance. Chem. Eng., 83(18):101, 1976.

27. Kem, R. Pressure Relief Valves for Process Plants. Chem. Eng., 84(5):187, 1977.

28. Isaacs, M. Pressure-Relief Systems. Chem. Eng., 78(5):113, 1971.

29. Kayser, D. S. Rupture Disc Selection. CEP, 68(5):61, 1972.

30. Britton, Stephen, Groth Equipment Corporation, Houston, Texas. Private communication with W. R. Phillips, Radian Corporation, Austin, Texas, May 19, 1980.

31. Beychok, Milton R. Wastewater Treatment. Hydrocarbon Processing, 50(12):110, 1971.

32. U.S. Environmental Protection Agency, Effluent Guidelines Division. Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category, final report. EPA-440/1-74-014a, Washington, D.C., April 1974.

33. Azad, H. S. ed. Industrial Wastewater Management Handbook. McGraw-Hill, New York, New York, 1976.

34. Jones, H. R. Pollution Control in the Petroleum Industry. Pollution Technology Review No. 4. Noyes Data Corporation, Park Ridge, New Jersey, 1973.

35. Long, J. and C. Murray. Industry Braces for New Water Cleanup Rules. C&EN, 57(20):31, 1979.

36. Sittig, M. Petroleum Refining Industry-Energy Saving and Environmental Control. Noyes Data Corporation, Park Ridge, New Jersey, 1978.

37. Little (Arthur D.), Inc. Environmental Consideration of Selected Energy Conserving Manufacturing Process Options, final report. Volume 4, Petroleum Refining Industry Report. EPA-600/7-076-034d, Washington, D.C., December 1976.

38. Thompson, S. J. Data Improves Separator Design. Hydrocarbon Processing, 52(10):81-83, 1973.

39. Kanter, C. V., et al. Emissions to the Atmosphere from Eight Miscellaneous Sources in Oil Refineries. Report No. 8, Joint District, Federal and State Project for the Evaluation of Refinery Emissions. Los Angeles County Air Pollution Control District, Los Angeles, California, 1958.

40. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division. Compilation of Air Pollution Emission Factors, 3rd edition, Supplement 8. AP-42, PB-275-525. Research Triangle Park, North Carolina, May 1978.

41. Hustvedt, K. C. and R. A. Quaney. Control of Refinery Vacuum Producing Systems, Wastewater Separators and Process Unit Turnarounds. EPA-450/2-77-025, OAQPS No. 1.2 - 081. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Office of Air and Waste Management, Research Triangle Park, North Carolina, October 1977.

42. Shaffer, N. R. and C. J. Seymour. Emissions of Hydrocarbons from Refineries in Los Angeles County. Los Angeles County, Air Pollution Control District, Los Angeles, California, April 1957.

43. Litchfield, D. K. Controlling Odors and Vapors from API Separators. Oil and Gas Journal, 69(44):60-62, November 1971.

44. Los Angeles, County of, Air Pollution Control District, et al. Emissions to the Atmosphere from Petroleum Refineries in Los Angeles County. Los Angeles, California, 1958.

45. Pojacek, R. B. Solid Waste Disposal-Solidification. Chem. Eng.,86(17):141-145, 1979.

46. Rosenberg, D. G., et al. Assessment of Hazardous Waste Practices in the Petroleum REfining Industry, final report. EPA/SW-129c. U.S. Environmental Protection Agency, June 1976.

47. Grove, G. W. Use Landfarming for Oily Waste Disposal Hydrocarbon Processing, 57(5):138-140, 1978.

48. Huddleston, R. L. Solid-Waste Disposal: Landfarming. Chem. Eng., 86(5):119-124, 1979.

3.0 CONTROL OF STACK AND OTHER PROCESS EMISSIONS

3.1 Sources of Emissions

Since no two refineries are exactly alike, refining process emissions vary considerably from site to site. In general, however, the major sources of atmospheric process emissions are sulfur recovery, fluid catalytic cracker catalyst regeneration, and process heaters and boilers.

The major types of atmospheric process emissions from refineries are hydrocarbons, sulfur oxides (SO_x), particulates, and carbon monoxide (CO). Process emission sources are categorized in Table E3-1 according to type of emissions.

Process heaters and boilers are used in a number of refinery processes. Instead of being discussed with each process, they are discussed collectively as a separate emission source.

3.1.1 Sulfur Recovery

The amount of sulfur in various product streams depends directly on the sulfur content of the crude oil. Sulfur tends to be more concentrated in the heavier cuts because of the low volatility of its compounds. The sulfur content of crude can vary from less than 0.1 weight percent to more than 5 weight percent. Any crude oil with more than 0.5 weight percent sulfur is generally considered sour and its products are subjected to sulfur removal processing.[1] If not removed, the sulfur can cause corrosion, pollution, and catalysis problems during refining or when the products are used as fuel or as petrochemical feedstocks.

TABLE E3-1. PROCESS EMISSIONS BY SOURCE AND TYPE

	Emissions						
Source	HC	Particulate	SO_x	CO	Aldehydes	NH_3	NO_x
Sulfur Recovery[a]			✓	✓			
Catalyst Regeneration (CO Boiler Vent)[a]	✓	✓	✓	✓	✓	✓	✓
Boilers and Process Heaters[a]	✓	✓	✓	✓	✓		✓
Vacuum Distillation[b]	✓						
Coking[b]	✓	✓					
Air Blowing[a]	✓						
Chemical Sweetening[b]	✓						
Acid Treating[b]	✓	✓					
Blowdown[b]	✓						
Compressor Engines[a]	✓	✓	✓	✓			

[a] Detailed results are in Appendix B.

[b] Not measured in this study.

Sulfur removal from whole crude is not generally economical.[2] Various intermediate stock streams routinely subjected to sulfur removal include the outlet streams from crude distillation and the cracking units.[3] The sulfur components in these streams are converted to hydrogen sulfide by contact with hydrogen over a nickel-molybdenum catalyst at an elevated temperature. The resulting H_2S boils between ethane and propane, so may be removed from the stream and concentrated by one of several means, the most common of which is absorption by monoethanolamine (MEA) or diethanolamine (DEA) followed by steam stripping.

At one time this H_2S was simply burned with other light gases as refinery fuel. In recent years, to minimize SO_x emissions and to produce elemental sulfur for sale to other industries, the Claus process has been used. The tail gas from a Claus unit is the main source of SO_x emissions in a refinery today. In the Claus process, some H_2S is oxidized to form SO_2 and water. Additional H_2S reacts with this SO_2 to form elemental sulfur and water.

The tail gas from a Claus unit contains H_2S, SO_2, CS_2, COS and sulfur. The emission rates of these sulfur compounds depend on the concentration of the H_2S stream to the Claus unit and the efficiency of that unit. Tail gas from a typical three-stage Claus unit, 95 to 96 percent efficient, can be expected to contain about 7,000 - 12,000 ppmv sulfur compounds.[4,5] The tail gas also contains carbon monoxide formed from small amounts of hydrocarbons and carbon dioxide in the feed stream. Since only partial oxidation of H_2S is desired, not enough oxygen is supplied to convert all the CO formed to CO_2. Typical compositions of the feed to a 94 percent efficient Claus unit and the tail gas stream from this unit are shown in Table E3-2. Claus tail gas is typically incinerated so that SO_x constitute the only sulfur compounds measurable in the final stack gas.

3.1.2 Catalyst Regeneration

Catalysts are used in several petroleum refining operations, namely, fluid catalytic cracking (FCC), moving bed catalytic cracking (TCC), catalytic hydrocracking, reforming, and various oil desulfurizations. These catalysts become coated with carbon and metals and must be regenerated to restore their activity. During regeneration, the carbon is oxidized to mixed carbon oxides and the hydrocarbons are burned incompletely.

In some applications, a catalyst must be regenerated only a few times a year. Emissions during regeneration may include catalyst fines, oil mist, hydrocarbons, ammonia, SO_x, chlorides, cyanides, NO_x, CO, and aerosols.[7] Though there may be significant emissions during the regeneration of one of these catalysts, the total emissions over the course of a year probably are not significant.

Catalytic cracking catalyst regeneration is a continuous process. Uncontrolled cracking catalyst regeneration emissions are one of the major sources of air pollution in a petroleum refinery. Flue gases from catalytic cracker regenerators contain particulates, SO_x, carbon monoxide, hydrocarbons, NO_x, aldehydes and ammonia.

Emission factors for the uncontrolled regeneration of FCC and TCC catalysts are reported in AP-42 and are listed here in Table E3-3. These factors are from a 1956 stack

TABLE E3-2. TYPICAL COMPOSITIONS OF FEED STREAM AND TAIL GAS FOR A 94 PERCENT EFFICIENT CLAUS UNIT

Component	Sour Gas Feed Volume %	Claus Tail Gas Volume %
H_2S	89.9	0.85
SO_2	0.0	0.42[b]
S_8 vapor	0.0	0.10 as S_1
S_8 aerosol	0.0	0.30 as S_1
COS	0.0	0.05
CS_2	0.0	0.05
CO	0.0	0.22
CO_2	4.6	2.37
O_2	0.0	0.00
N_2	0.0	61.04
H_2	0.0	1.60
H_2O	5.5	33.00
H.C.	0.0	0.00
	100.0	100.00
Temperature, °F	104	284
Pressure, psig	6.6	1.5
Total Gas Volume[a]	--	3.0 × feed gas volume

[a] Gas volumes compared at standard conditions.

[b] NSPS requires an emission of less than 250 ppmv (0.025%) SO_2, zero percent O_2, dry basis if Claus Unit Tail Gas is oxidized as the last control step, or, 300 ppmv SO_2 equivalent reduced compounds (H_2S, COS, CS_2) and only 10 ppm H_2S as SO_2, zero percent O_2, dry basis, if the Tail Gas is reduced as the last control step.

Source: Reference 6.

sampling survey of FCC and TCC units in Los Angeles County.[8] The survey involved six FCC units (with a total fresh feed rate of 157,000 BPD) and nine TCC units (with a total fresh feed rate of 69,300 BPD).

TABLE E3-3. EMISSION FACTORS FOR UNCONTROLLED REGENERATION OF THE CATALYTIC CRACKING CATALYST

	Emission Factor (lb/1,000 bbl Fresh Feed)						
Source	Particulates	SO_x as SO_2	CO	Total HC	NO_x as NO_2	Aldehydes	NH_3
Fluid Catalytic Cracking (FCC)	242	493	13,700	220	71	19	54
Moving Bed Catalytic Cracking (TCC)	17	60	3,800	87	5	12	6

Source: Reference 5.

These factors indicate that the uncontrolled emissions from FCC units are several times worse than from TCC units ("uncontrolled" here is defined as the catalyst regenerator off gas with conventional regeneration prior to any external control). Radian believes that this conclusion is incorrect for particulate emissions and that the factors for other emissions should be reviewed.

The effect of passing the FCCU regenerator flue gas through a CO boiler can be seen in Tables E3-4 and E3-5.

TABLE E3-4. EMISSION RATES FROM FCCU REGENERATORS, BEFORE AND AFTER CO BOILER

Chemical Species[a]	Composition of Flue Gas from FCCU Without CO Boiler (Reference 9)	Emissions from FCCU Equipped With CO Boilers Regenerator Flue Gas Composition	
		Reference 9	This Study[b]
SO_2, ppmv	130-3300	$\leq$ 2700	14-871
SO_3, ppmv	NA[c]	NA[c]	0.7- 13.5
NO_x (as NO_2), ppmv	8-394	$\leq$ 500	94-453
CO, Vol.%	7.2-12.0	0-14	0.0
CO_2, Vol.%	10.5-11.3	11.2-14.0	13.5-16.1
O_2, Vol.%	0.2-2.4	2.0-6.4	3.2-7.0
N_2, Vol.%	78.5-80.3	82.0-84.2	77.0-82.7
H_2O, Vol.%	13.9-26.3	13.4-23.9	9.2-22.7
Hydrocarbons, ppmv	98-1213	NA[c]	0-46
Ammonia, ppmv	0-675	NA[c]	0-15
Aldehydes, ppmv	3-130	NA[c]	0-20
Cyanides, ppmv	0.19-0.94	NA[c]	0-19
Particulates, gr/SCF	0.08-1.39	0.017-1.03	0.012-0.304
Temp., °F	1000-1200	458-820	386-727

[a] All considerations on dry basis
[b] Based on sampling of 6 stacks
[c] Not available

TABLE E3-5. EMISSION RATES FROM FCCU REGENERATORS EQUIPPED WITH CO BOILERS

	Total Emission Rate Based on Data From This Study,[a] Pounds Emitted per 1000 bbl Fresh Feed to FCCU		
Gas Components	Range of Emission Rates	Mean Emission Rate	Median Emission Rate
SO_2	8-382	196	162
SO_3	0.5-9.0	2.9	1.0
NO_x (as NO_2)	41-193	89	71
CO	0	0	0
Hydrocarbons	1.1-12.0	5.1	2.5
Ammonia	0.06-1.65	0.56	0.21
Aldehydes	0.0-4.6	2.0	1.8
Cyanides	0.001-4.54	0.84	0.11
Particulates	7.9-45.2	23.2	17.0

[a] Based on Sampling of 6 Stacks

The amount of CO is reduced, of course. However, another noticeable result is the substantial reduction in emissions of hydrocarbons, ammonia, and aldehydes. The exiting flue gas temperature is much lower after passing through the CO boiler.

3.1.3 Boilers and Process Heaters[10]

Most refineries use steam boilers to provide steam for direct use in various processes, for heating and for driving steam turbines. Large amounts of steam are needed for light end strippers, vacuum steam ejectors, process heat exchangers and reactors. About 40 pounds of steam are required by a typical refinery per barrel of refining feed. This steam demand requires a boiler size of 53,000 Btu per barrel of refining feed. Some steam is also generated in waste heat boilers, the largest of which is, in some refineries, a carbon monoxide boiler used to control emissions from the regeneration of the catalytic cracking catalyst. Most steam production facilities associated with processes produce low pressure steam.

Process heaters are used extensively in refining operations. They are the largest combustion source of hydrocarbons in a refinery. The total process heater demand in a modern refinery is approximately 270,000 Btu per barrel of refining feed. Older, less efficient refineries may require up to 600,000 Btu per barrel of refining feed.

Refinery boilers and heaters are fired with the most available fuel, usually purchased natural gas, refinery fuel gas (mostly methane), or residual fuel oil. Ordinarily, the refinery gas supplies about half the fuel needs. Natural gas is used in the summer months and residual oil in the cooler months when natural gas supplies go to preferred residential customers.

Emissions from boilers and process heaters depend on the operating parameters of the unit and the fuel burned. Emission factors for burning natural gas and residual fuel oil are given in Table E3-6.

TABLE E3-6. EMISSIONS FROM REFINERY BOILERS AND HEATERS

	Fuel	
Pollutant	Natural Gas $lb/10^6$ SCF	Fuel Oil $lb/10^3$ gal
Hydrocarbons (as CH_4)	3	1
Particulates	5-15	--[a]
SO_x as SO_2	0.6[b]	157S[c]
CO	17	5
NO_x as NO_2	120-130[d]	60[e]

[a] A function of fuel oil grade and sulfur content - For Grade 6: $lb/10^3$ gal - 10S + 3; For Grade 4: 7 $lb/10^3$ gal; For Grade 5: 10 $lb/10^3$ gal.

[b] Based on average sulfur content of natural gas of 2,000 $gr/10^6$ Std Ft^3.

[c] S equals percent by weight of sulfur in fuel.

[d] Use first number for tangentially fired units, second for horizontally fired units.

[e] Strongly dependent on the fuel nitrogen content.

Source: Reference 5

In addition to the combustion emissions, there are also emissions associated with the decoking of the heaters. At intervals of about six months to three years, each heater must be flushed with a steam-air mixture to remove the interior coke deposits. Emissions are similar to those from decoking the delayed coking unit, but they are smaller and more infrequent.

3.1.4 Vacuum Distillation

After the crude oil has been separated in an atmospheric tower, the bottoms are transferred to a vacuum distillation tower for further separation. Vacuum distillation separates the heavy residue from the atmospheric distillation into a heavy residual oil and one or more heavy gas oil streams. This is accomplished at lower temperatures than would be required at atmospheric pressure and avoids excess thermal cracking of heavier materials.[11]

Vacuum fractionators are maintained at approximately 0.2 to 0.8 psia by either steam ejectors or mechanical vacuum pumps.[1] A major portion of the vapors withdrawn from the column by the ejectors or pumps is recovered in condensers. Approximately 50 pounds of noncondensable hydrocarbons are emitted per 1,000 barrels of vacuum unit charge when barometric condensers are used. This corresponds to approximately 18 pounds of hydrocarbon emissions per 1,000 barrels of refinery feed.[5] Quantities of noncondensable vapors as high as 130 pounds per 1,000 barrels of charge have been recorded.[12]

3.1.5 Coking

Coking processes convert low value residual oil into higher value gas oil and coke by cracking the residual oil at a high temperature and atmospheric pressure. There are two accepted methods for coking: fluid coking and delayed coking. Delayed coking is the long standing, more widely used method; fluid coking is expected to increase in importance in the next few years. Each process has advantages and disadvantages relative to the other.

In the delayed coking process, the feed stream is heated and transferred to a coke drum which provides the proper residence time, pressure, and temperature for coking. When the coke drum has been filled to capacity with coke, the coke is cut from the walls with high-pressure water. Hydrocarbons and particulates are emitted when coke is removed from the drums.

Fluid coking is a continuous process in which the feed is injected into a fluidized bed of hot coke particles. The hot oil is cracked and a thin layer of new coke is deposited on the particles. The coke particles travel to a burning chamber where approximately one fourth of the coke is burned for process heat. Since more coke is produced than burned, a net coke product stream is produced. Approximately 30 pounds of carbon monoxide and about 520 pounds of particulates per 1,000 barrels of feed are emitted from an uncontrolled fluid coking unit.[5,13] There are often additional pollutants from coke combustion such as SO_x, NO_x, and organics.

3.1.6 Air Blowing

Blowing air through a material may serve one of several purposes: to oxidize, to remove moisture, to strip spent chemicals, or to mix. The amount of emissions produced by air blowing depends on the amount of air used per ton of charge, the volatility of the charge, and the temperature of the operation. In all of its uses, uncontrolled air blowing produces noxious odors.

3.1.6.1 Asphalt Blowing

Air is sometimes blown through asphalt to oxidize it and, therefore, increase its melting temperature and its hardness. High temperatures are used to promote the oxidation.

The vent gases from asphalt blowing were the most objectionable form of air pollution in a petroleum refinery before control procedures became commonplace.[3] The operating conditions are favorable for the production of extremely undesirable polynuclear aromatics.

Emissions from asphalt blowing are lessened by the fact that asphalt material is distilled at high temperatures before it is subjected to asphalt blowing. Available data indicate uncontrolled emissions from asphalt blowing to be 40 to 80 pounds of hydrocarbons per ton of asphalt treated.[12]

3.1.6.2 Air Blowing of Gas Oils

Air blowing of gas oil products to remove moisture takes place in a packed tower or vessel. Operating temperatures are kept low to minimize loss of the gas oil and to prevent oxidation or degradation of the product. The exhausted gas does, however, contain the lighter hydrocarbon components of the gas oil.

3.1.7 Chemical Sweetening

Chemical sweetening rids hydrocarbons of odorous mercaptans. Only low-sulfur (sweet) materials are subjected to this treatment; more drastic sulfur removal methods such as hydrodesulfurization are used for high sulfur (sour) materials. The mercaptans may be removed from the material (extractive sweetening) or converted to disulfides (oxidative sweetening).

In extractive sweetening, an aqueous NaOH or KOH solution extracts the sulfur. The spent caustic solution may be regenerated by steam blowing or steam-air blowing, or it may be disposed of. Before disposal, hydrocarbons are removed from the solution by inert-gas stripping. This inert-gas stripping may be a source of hydrocarbon emissions.

Catalysts are used to promote oxidative sweetening; air is the oxidizing agent. Air is also used to regenerate the catalyst. Hydrocarbon emissions may results from both the oxidation and the regeneration steps.

3.1.8 Acid Treating

Hydrocarbon streams may be treated with acid to remove or dissolve undesirable materials, or convert them to a more desirable form. The stream is contacted with the acid and mixed thoroughly to form an emulsion. Air blowing is sometimes used to agitate the mixture.

The use of sulfuric acid results in a hydrocarbon/acid sludge which is removed by clay filtration. To recover the acid, the sludge may be incinerated and the resultant SO_2 used to produce more sulfuric acid. Alternatively the hydrolysis-concentration process may be used. In this process, hot gases from the combustion of oil or gas are bubbled through the sludge to volatilize the hydrocarbon dilutent and to concentrate the acid. Off-gases pass through a mist eliminator to the atmosphere. These gases may contain hydrocarbons and SO_2.

3.1.9 Blowdown

Periodic maintenance and repair of equipment is essential to the refining operation. All units and equipment subject to shutdowns, upsets, emergency venting, or purging are manifolded into a multi-pressure collection system. Discharges into the system are segregated according to their operating pressures, then separated into vapor and liquid cuts.

Because the blowdown system receives materials from all processing units within the plant, any volatile material found in any process stream may be emitted from an uncontrolled blowdown system. The emission rate is a function of the number of equipment items manifolded into the system and the frequency of equipment discharges. It is estimated that 580 pounds of hydrocarbons are emitted from an uncontrolled blowdown system per 1,000 barrels of refining feed.[5]

3.1.10 Compressor Engines

Reciprocating and gas turbine engines fired with natural gas or refinery fuel gas are often used in older refineries to run high-pressure compressors. These units are less reliable and harder to monitor than steam turbines or electric motors. These factors, along with increased prices of natural gas, will probably cause a decline in the use of these engines.[10]

The exhaust emissions from these engines include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes, and depending on the sulfur content of the fuel, sulfur compounds. Emission factors for reciprocating and gas turbine compressor engines fired with natural gas are given in Table E3-7. Particulate values were not available.

TABLE E3-7. EMISSION FACTORS FOR RECIPROCATING AND GAS TURBINE COMPRESSOR FUELED WITH NATURAL GAS

	Pollutant, $lb/10^3\ ft^3$ gas burned			
Engine Type	NO_x as NO_2[a]	CO	HC as C[b]	SO_x as SO_2[c]
Reciprocating	3.4	0.43	1.4	2S
Gas Turbine	0.3	0.12	0.02	2S

[a] At rated load. In general, NO_x emissions increase with increasing load and intake air temperature. They generally decrease with increasing air-fuel ratios and absolute humidity.

[b] Overall less than one percent by weight is methane.

[c] S = Refinery gas sulfur content (lb/1,000 SCF): factors based on 100% combustion of $S \rightarrow SO_2$.

Source: Reference 5

3.2 Control Technology

Most of the process emissions described in Section 3.1 can be controlled. This section describes control methods that are used now or that could be used by the industry.

"Existing" controls included in Section 3.2.1 are those considered to be in relatively common usage. "Available" controls included in Section 3.2.2 are those which have had only limited application and those which have not yet been applied in the refining industry. Controls which have been used in other industries and which might be applicable for the refining industry are included in Section 3.2.3.

3.2.1 Existing Levels of Control in Refineries

Existing controls for each process emission source are discussed in this section. Because incinerators and flares are applicable to several emission sources, they are discussed in detail in Section 3.2.1.1 and 3.2.1.2.

3.2.1.1 Incineration

Incineration is an accepted method for disposal of combustible wastes. It is most useful when the heat generated during combustion can be used to offset other plant energy needs.

Three types of incinerators used in refineries are existing process heaters and boilers, thermal incinerators, and catalytic incinerators. Particle collection devices are often used on the flue gases from incinerators.

Boilers Used as Incinerators--Fireboxes of boilers and fired heaters can be potential incinerators (afterburners) if the temperature, turbulence, and flame contact are adequate to volatilize and burn the combustible contaminants. If the waste volatile organics have appreciable heating value, the firebox must be specially designed to take advantage of this heat potential; such units are known as waste heat boilers. If the heat content of the waste gas is low, common steam and hot water heaters and boilers are used.

Successful adaptation of boilers for use as afterburners is not common. The primary function of a boiler is to supply steam or hot water. Its use as an air pollution control unit may interfere with that function.

Satisfactory use of boilers as afterburners is possible only if the following conditions exist:

- The boiler operates when the pollution source is operated.
- Temperature, turbulence, and residence time within the firebox are sufficient for complete combustion.
- The air contaminants are wholly combustible (otherwise, boiler efficiency and steam generation may be reduced from deposits on the process heater internals).
- The products of combustion are compatible with the boiler construction materials.

Thermal Incineration--Thermal incinerators are used for most refinery waste gases. They usually eliminate more than 95 percent of the organic vapor present.[10] For combustion of organic vapors and liquids, the concentrations of vapor and air must be within the limits of flammability, termed the upper and lower explosive limits (UEL and LEL, respectively). These limits differ for various hydrocarbon compounds. When concentrations of combustibles are less than LEL, supplemental heat is required to initiate combustion.

An efficient thermal afterburner design must provide for:

- An adequate residence time for completion of the combustion process.
- Sufficiently high temperature in the afterburner for the complete oxidation of the combustibles.
- Adequate velocities to insure good mixing without quenching combustion.

If combustion is inhibited by insufficient temperature, insufficient residence time, or poor mixing, then carbon monoxide, aldehydes, and other products of incomplete combustion may result.

Burner type and arrangement affect combustion rates and residence time. The more thorough the contact of flame with the waste stream, the shorter the time required for complete combustion. Burner placement depends not only on the burner type, but also on the design requirement for intimate contact of the combustible gases with the burner flame. Maximum efficiency occurs when all of the combustible matter passes through the burner. Multijet and mixing-plate burners provide the most effective flame contact. Maintaining high turbulence or injecting steam also promotes the intimate contact necessary for complete combustion.

Most refinery waste gases can be satisfactorily incinerated at 1,150° to 1,400°F with a residence time of 0.2 to 0.7 seconds.[14]

In thermal afterburners, the organic vapor stream is delivered to the refractory-lined burner area by either the process exhaust system or by a blower. The combustible gases are mixed thoroughly with the burner flames in the upstream part of the chamber and then pass through the remaining part of the chamber where the combustion process is completed.

Natural gas, LPG, distillate fuel oil, and residual fuel oils are used to fuel afterburners. Oil flames are longer than gas flames and thus require longer fireboxes. The combustion of fuel oils produces sulfur oxides and particulates which may cause corrosion and soot accumulation on afterburner internals and heat transfer surfaces.

Heat recovery from the hot cleaned gases offers a way to reduce the afterburner energy requirements at the expense of increased equipment costs. The simplest application is to use the hot cleaned gases exiting the afterburner to preheat cooler process gases entering the afterburner. This arrangement is termed primary heat recovery. In designing heat recovery systems, consideration should be given to potential safety problems. Explosions or fires may occur in the heat exchanger from process upsets or from accumulation of flammable liquids or dust in the exchanger.

With secondary heat recovery, exhaust from the primary heat exchanger supplies energy which can be used elsewhere in the plant. Secondary heat recovery can have a major effect on energy economics when used to supply steam, hot water, or process heat to facilities located near the incinerator. Optimum application occurs when heat utilizing equipment is operated on the same schedule as the afterburner.

Catalytic Incineration--The use of catalytic incineration is not widespread in refineries.[14] Cost of catalyst versus cost of fuel must be considered along with possible fouling of the catalyst by components of the waste gas. Very dilute streams with foul odors are the most likely candidates for catalytic incineration.

When a preheated gas stream is passed through a catalytic afterburner, the catalyst bed initiates and promotes oxidation. The combustion reaction occurs at a significantly lower temperature than that of direct flame combustion; however, care must be taken to assure that combustion is complete. Catalytic afterburners offer the advantage of lower fuel costs in some applications; however, the relative fuel savings diminish as primary and secondary heat recovery are added to thermal afterburners. Construction materials for catalytic incinerators costs may also be lower because of the reduced temperatures.

Combustion catalysts include platinum, platinum alloys, copper chromite, copper oxide, chromium, manganese, nickel, and cobalt. These are deposited in thin layers on an inert substrate. Available substrate shapes include rods, honeycombs, and ribbons designed to provide catalyst surface area.

For a catalyst to be effective, "active sites" upon which the organic gas molecules can react must be accessible. The buildup of condensed polymerized material or particles prevents contact between active sites and the gases ("deactivation"). A catalyst can be "reactivated" by removing the coating; cleaning methods vary with the catalyst. Deactivation also occurs through reaction of the catalyst metal with phosphorous, bismuth, arsenic, antimony, mercury, lead, zinc, or tin. Gas streams containing these elements are best treated by thermal incineration. Sulfur and halogens are also "poisonous" to the catalyst, but their effects are reversible.

Catalyst material can be lost from the support by erosion and attrition and by vaporization at high temperatures. To protect the catalyst from overheating, volatile organic concentrations are usually limited to 25 percent of the lower flammability limit. Most combustion catalysts cannot be operated at temperatures greater than 1,000 - 1,200°F.

Particulate Control Devices--Many kinds of wastes other than refining gases may be incinerated, such as garbage, contaminated and combustible liquids and semifluid sludges. Flue gases from the combustion of these materials may contain excessive amounts of particles which must be removed. The methods commonly used to remove particles from flue gases are cyclones and electrostatic precipitators.

Cyclones - A cyclone consists of a cylinder with a tangential opening through which the particle-bearing gas enters at a high velocity, creating a centrifugal force. As the particles strike the walls of the cylinder, they slide down it. At the bottom of the cyclone is the dipleg, essentially a hollow pipe through which the particles exit the cyclone.

Cyclones have no moving parts and use no fuel or electricity. However, they cannot handle large volumes of air effectively. When large volumes of air must be processed, many small cyclones may be used or air may be sent through several cyclones in series.

Cyclones are most effective for particles larger than 40 microns. Efficiency drops drastically for smaller particles: cyclones can collect 90 percent by weight of particles larger than 10 microns, but only 60 percent by weight of particles smaller than 5 microns.[15]

Electrostatic precipitators - An electrostatic precipitator is a device that removes particles from a gas stream by giving them electrical charges (from a discharge electrode) and then applying an electrostatic force that causes them to move toward electrically grounded collecting electrodes. There, the fine particles are agglomerated and dislodged to fall into a hopper below.

As opposed to a cyclone, an electrostatic precipitator can process very large volumes of gas (50,000 to 2,000,000 acfm) and very efficiently remove particles as small as 0.05 micron.[14]

However, electrostatic precipitators are very large and their initial and total annual operating costs are quite high. They are used only when essential for meeting air pollution control regulations and usually are installed in series after several high efficiency cyclones.[14]

3.2.1.2 Flaring

Flares are used most often as safety devices to dispose of waste streams which cannot be economically recovered or used as fuel. They are usually unsuitable for the treatment of dilute gas streams because of the cost of supplemental fuel needed to attain the minimum combustion temperature. They are also generally less effective than other devices for controlling organic vapors because of the considerable quantities of carbon monoxide that may be produced.

Almost complete combustion of organic gases and vapors can be achieved with a flare if the gas has sufficient heat value to attain the minimum temperature necessary for combustion and if it is adequately mixed with an adequate supply of air. However, not all of the hydrocarbons are completely oxidized to carbon dioxide and water. As much as ten percent of the combustion mixture may be carbon monoxide.[16]

NO_x emissions from flares are also common due to direct contact of nitrogen with oxygen at the flame temperature. A typical emission rate for a flare system in a petroleum refinery is 19 lb $NO_x/10^3$ bbl refinery feed.[5]

Other air contaminants emitted from flares vary with the composition of gases burned. Sulfur dioxide is produced from the combustion of sulfur compounds such as hydrogen sulfide in the flare gas. However, high toxicity and low odor threshold make venting of hydrogen sulfide to a flare an undesirable and sometimes dangerous method of disposal.

An insufficient air supply produces a smoky flame. Within the reducing atmosphere of the smoke, hydrocarbons can crack to elemental hydrogen and carbon or can react to form polymers. Side reactions become more pronounced as the molecular weight and unsaturation of the inlet gas increase. Olefins, diolefins, and aromatics characteristically burn with smoky, sooty flames as compared to paraffins and naphthenes.

There are three types of flares for the disposal of waste gases: elevated flares, ground-level flares, and burning pits.

Elevated Flares--An inert gas is injected into the combustion zone of elevated flares to provide smokeless operation. Steam is most commonly used for this purpose for elevated flares. Steam injection provides the following benefits:

- Energy available at relatively low cost can be used to inject air and provide turbulence within flame.

- Steam and/or water react with the gas to form oxygenated compounds that burn readily at relatively low temperatures.

- Steam retards polymerization by reducing the partial pressure of the fuel.

There are alternate methods for obtaining smokeless operation in an elevated flare when the use of steam is uneconomical or presents problems such as freezing in cold climates. The alternative methods are compressed air injection, water spray, high-pressure gas injection, air blower, and high turbulence tips. In general, these methods are not used if the use of steam is practical.

There are three types of elevated steam-injected flares which vary with the manner in which the steam is injected into the combustion zone.

In the first type, steam is injected by several small jets placed concentrically around the flare tip. The jets are installed at an angle and cause the steam to discharge in a converging pattern immediately above the flare tip.

A second type has a flare tip with no obstruction to flow. The flare tip is the same diameter as the stack. The steam is injected by a single nozzle located concentrically within the burner tip. In this type of flare, the steam is premixed with the gas before ignition and discharge.

A third type is equipped with a flare tip that promotes turbulence by causing the gases to flow through several tangential openings. A steam ring at the top of the stack has numerous equally spaced holes for injecting steam into the gas stream.

The injection of steam into a flare can be controlled either manually or automatically. In some installations, the steam is supplied at maximum rates, and manual throttling of the steam is required for a particular gas flow rate. For the best combustion with minimum steam consumption, instrumentation should be provided which automatically controls the steam rate based on the gas flow rate.

Ground-level Flares--A ground-level flare is usually designed for daily process needs with the high flows during major emergencies routed to an accompanying elevated flare. Ground-level flares are of four principal types: horizontal venturi, water injection, multijet, and vertical venturi.

A horizontal venturi flare system utilizes groups of standard venturi burners. In this type of burner, the gas pressure inspires combustion air for smokeless operation.

A water-injection flare consists of a single burner with a water spray ring around the burner nozzle. Air is drawn in as a result of the spray action and the water vapor provides for the smokeless combustion of gases. Water is not as effective as steam for controlling smoke with high gas-flow rates, unsaturated material, or wet gases.

A multijet ground flare uses two sets of burners, one for normal gas release rates and both for higher flaring rates.

A vertical, venturi ground flare also uses commerical-type venturi burners. This type of flare is suitable for relatively small flows of gas at a constant rate.

Burning Pits--Burning pits are reserved for extremely large gas flows caused by catastrophic emergencies in which the capacity of the primary smokeless flares is exceeded. Ordinarily, the main gas header to the flare system has a water seal bypass to a burning pit. Excessive pressure in the header blows the water seal and vents the vapors and gases to the burning pit for combustion.

3.2.1.3 Sulfur Recovery

The Claus unit is the accepted method for sulfur recovery in a modern refinery. However, because it is not totally efficient in producing elemental sulfur, it is a major source of emissions. Much progress has been made in recent years in the control of emissions from Claus units. This discussion will consider first the Claus unit itself, then methods for cleaning up the Claus unit tail gas.

More than 70 methods have been proposed for treatment of the Claus unit tail gas.[17] These methods may be continuations of the Claus reaction or add-on processes with chemistry quite different from that of the Claus reaction. Incineration is sometimes used alone to clean Claus unit tail gas, sometimes to prepare the tail gas for further treatment, and sometimes after that treatment.

The six tail gas clean-up methods discussed in this section are those considered the most viable at present in light of energy demands, economics, and effectiveness. The first three processes--Amoco's CBA Process, the Sulfreen Process, and the IFP Process--are continuations of the Claus reaction under more favorable conditions. The second three processes--the Beavon Process, the SCOT Process, and the Wellman-Lord Process--are add-on units with higher efficiencies than the first three. These six methods are outlined briefly in Table E3-8.

Because incineration is used with several of these methods, it is discussed in the section "Incineration of Claus Unit Tail Gas," immediately after the discussion of the Claus unit itself.

The Claus Process--Because of its economic advantages, a Claus unit for the conversion of H_2S to elemental sulfur is often considered as simply part of normal refining operations. It is the source of the purest elemental sulfur. It is cited as a major source of air pollution; but, it must be recognized as a very effective control device.

The Claus process works best for gas streams containing greater than 20 volume percent H_2S and less than 5 volume percent hydrocarbons.[1] There are several flow schemes available according to the H_2S content of the feed stream of the unit. In any case, the overall Claus reaction is as follows:

$$H_2S + \frac{1}{2} O_2 \Rightarrow \frac{1}{2} S_n + H_2O \qquad (1)$$

TABLE E3-8. EXISTING METHODS FOR REMOVAL OF SULFUR FROM CLAUS TAIL GAS

Name	Developer	Description	Final Tail Gas S Concentration	Product	Cost (% Cost of Claus)
CBA	Amoco	Claus reaction continued at low temperature; removal of condensed sulfur drives reaction. Bed regenerated with hot gas from Claus unit.	1500 ppmv S	S_o	50-150%
Sulfreen	SNPA/Lurgi	Claus reaction continued at low temperature as in CBA. Bed regenerated with hot nitrogen.	1500-2000 ppm S	S_o	50-150%
IFP-1500	Institut Francais du Petrole	Claus reaction occurs in a solvent.	1000-2000 ppm S	S_o	variable
BSRP	Ralph M. Parsons & Union Oil Co. of California	All sulfur compounds reduced to H_2S which is processed in a Stretford unit.	250 ppm S or less	S_o	100%
SCOT	Shell	All sulfur compounds reduced to H_2S which is recycled to Claus	200-500 ppmv H_2S	Feed to Claus	75-100%
Wellman-Lord	Wellman Power Gas	SO_2 in incinerator gas contacted with Na_2SO_3 to form $NaHSO_3$. Na_2SO_3 regenerated in evaporator/crystallizer.	<200 ppmv SO_2	Na_2SO_4/Na_2SO_3 crystals	130-150%

where n represents the various molecular forms of sulfur vapor. The two most popular designs are illustrated in Figure E3-1. In the "once-through" design, the incoming H_2S-rich stream is burned in a limited amount of air to convert one-third of the H_2S to SO_2 according to the following reaction:

$$2\ H_2S + 2\ O_2 \rightarrow SO_2 + S + 2\ H_2O \tag{2}$$

The hot gases from this reaction are then passed over a bauxite, alumina, or cobalt molybdenum catalyst to react the sulfur dioxide with unburned H_2S:

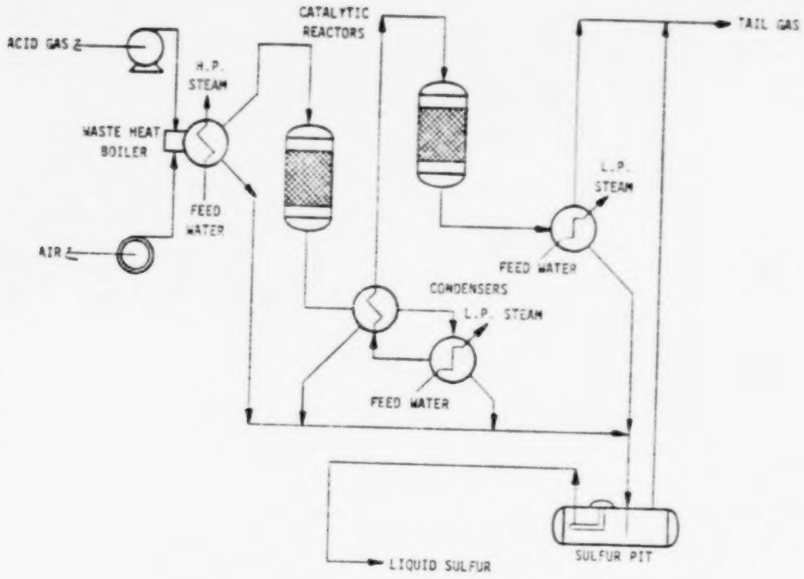
$$2\ H_2S + SO_2 \rightarrow 3\ S + 2\ H_2O \tag{3}$$

If the "split-stream" or by-pass," design is used, one-third of the incoming stream is separated and burned more completely according to the following reaction:

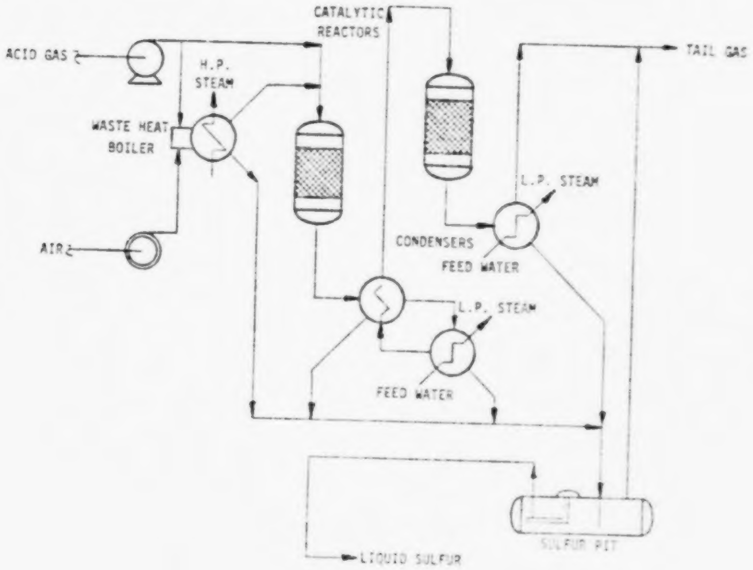
$$H_2S + \frac{3}{2}\ O_2 \rightarrow SO_2 + H_2O \tag{4}$$

The remaining H_2S is reacted over a catalyst with the hot gas from the furnace to form elemental sulfur according to reaction (3).

The "direct oxidation" design is for streams with lower concentrations of H_2S. In this design, the incoming stream is preheated, mixed with air, and then passed over the bauxite or alumina catalyst.


CATALYTIC REACTORS
TAIL GAS
ACID GAS
H.P. STEAM
WASTE HEAT BOILER
FEED WATER
AIR
L.P. STEAM
FEED WATER
CONDENSERS
L.P. STEAM
FEED WATER
LIQUID SULFUR
SULFUR PIT

STRAIGHT THROUGH CLAUS PROCESS


CATALYTIC REACTORS
TAIL GAS
ACID GAS
H.P. STEAM
WASTE HEAT BOILER
AIR
L.P. STEAM
CONDENSERS
FEED WATER
L.P. STEAM
FEED WATER
LIQUID SULFUR
SULFUR PIT

SPLIT FLOW CLAUS PROCESS

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Figure E3-1. The Claus Process.

Two side reactions produce relatively inert forms of sulfur when any of the designs are used:

$$CH_4 + 4S \rightarrow CS_2 + 2\ H_2S \tag{5}$$

$$CO_2 + H_2S \rightarrow COS + H_2O \tag{6}$$

The CS_2 and COS are usually passed unchanged to the tail gas. They can account for 0.25 to 2.5 percent of the sulfur content of the tail gas.[18] However, with proper design, including the use of the cobalt molybdenum catalyst and a higher inlet temperature for the first reactor, the CS_2 and COS concentrations in the tail gas can be minimized.[4]

The choice of Claus unit design depends on the concentrations of H_2S and other components such as hydrocarbons, water vapor, and CO_2 in the feed streams. For instance, the "split-stream" design efficiently suppresses the undesirable formation of COS when the incoming stream contains 30 percent or more CO_2.[19] Hydrocarbons can seriously affect the operation of the unit.[20]

The Claus designs described above with one pass through the catalyst reactor convert 80 to 86 percent of the H_2S to elemental sulfur.[1,21] This efficiency can be greatly enhanced by repeating the catalytic stage one or more times. Two-stage Claus units can achieve 92 to 95 percent efficiency; three stages, 95 to 96 percent; and four stages, 96 to 97 percent.[5] Conversion is ultimately limited by the reverse reaction. Recovery percentages for various feed compositions are given in Table E3-9.

TABLE E3-9. TYPICAL CLAUS PLANT SULFUR RECOVERY FOR VARIOUS FEED COMPOSITIONS

Hydrogen Sulfide in Sulfur Plant Feed (dry basis) (%)	Calculated Percentage Recovery[a]		
	Two Reactors	Three Reactors	Four Reactors
20	92.7	93.8	95.0
30	93.1	94.4	95.7
40	93.5	94.8	95.1
50	93.9	95.3	96.5
60	94.4	95.7	96.7
70	94.7	96.1	96.3
80	95.0	96.4	97.0
90	95.3	96.6	97.1

[a] Assumes 1 mole percent hydrocarbon contamination, conventional temperature and reheat techniques, average organic by-products and entrainment allowance.

Source: Reference 20.

These efficiencies, once considered sufficient, do not meet new regulations. Further treatment of the Claus unit tail gas is discussed in succeeding sections.

Claus plant costs are sensitive to the flow rate and composition of the input stream as well as the sulfur removal efficiency. It is difficult to generalize the costs. As an example, however, the capital investment costs for a Claus plant having a capacity of 250×10^6 ft^3/day of gas are \$14 $\times 10^6$ (construction period is 4th quarter 1979 through 4th quarter 1980). This plant has a sulfur removal efficiency of about 95 percent.

Incineration of Claus Unit Tail Gas--The tail gas from the Claus unit is often incinerated either before it passes to the atmosphere or is subjected to further treatment. This incineration takes place at temperatures of about 950 to 1,200°F or above in refractory lined vessels with one or more burners.

An auxiliary fuel supply such as natural gas or fuel oil provides the heat necessary for incineration since the heating value of the tail gas is low. Excess air levels of 20 to 100 percent are used.

The objective of tail gas incineration is to convert all sulfur compounds in the tail gas to SO_2, but this conversion is not complete. Typical compositions of a sour gas feed stream and the corresponding Claus tail gas before and after incineration are given in Table E3-10.

The Amoco Cold Bed Absorption (CBA) Process[17,22,23]-- As stated in "The Claus Process" section, the completion of the Claus reaction is ultimately limited by the reverse reaction. The Amoco CBA process carries the Claus reaction nearer to completion by condensing out the elemental sulfur as it is formed. The Claus reaction is continued in a separate reactor over the conventional Claus catalyst at temperatures (260 to 300°F) below the dew point of sulfur. Gas from the reactor is then incinerated.

The condensation of sulfur gradually reduces the activity of the catalyst. There are two reactors so that one can be regenerated while the other is operating. To regenerate the catalyst, hot gas from the first Claus reactor is passed through the bed. The sulfur is vaporized and condensed in

TABLE E3-10. TYPICAL COMPOSITIONS OF FEED STREAM AND TAIL GAS STREAMS FROM A 94 PERCENT EFFICIENT CLAUS UNIT AND INCINERATION

Component	Sour Gas Feed Volume %	Claus Tail Gas Volume %	Thermally Incinerated Tail Gas Volume %
H_2S	89.9	0.85	0.001
SO_2	0.0	0.42	0.89
S_8 vapor	0.0	0.10 as S_1	0.00
S_8 aerosol	0.0	0.30 as S_1	0.00
COS	0.0	0.05	0.02
CS_2	0.0	0.05	0.01
CO	0.0	0.22	0.10
CO_2	4.6	2.37	1.45
O_2	0.0	0.00	7.39
N_2	0.0	61.04	71.07
H_2	0.0	1.60	0.50
H_2O	5.5	33.00	18.57
H.C.	0.0	0.00	0.00
	100.0	100.00	100.00
Temperature, °F	104	284	752
Pressure, Psig	6.6	1.5	0
Total gas volume[a]	---	3.0 x feed gas volume	5.8 x feed gas volume

[a] Gas volumes compared at standard conditions

Source: Reference 6

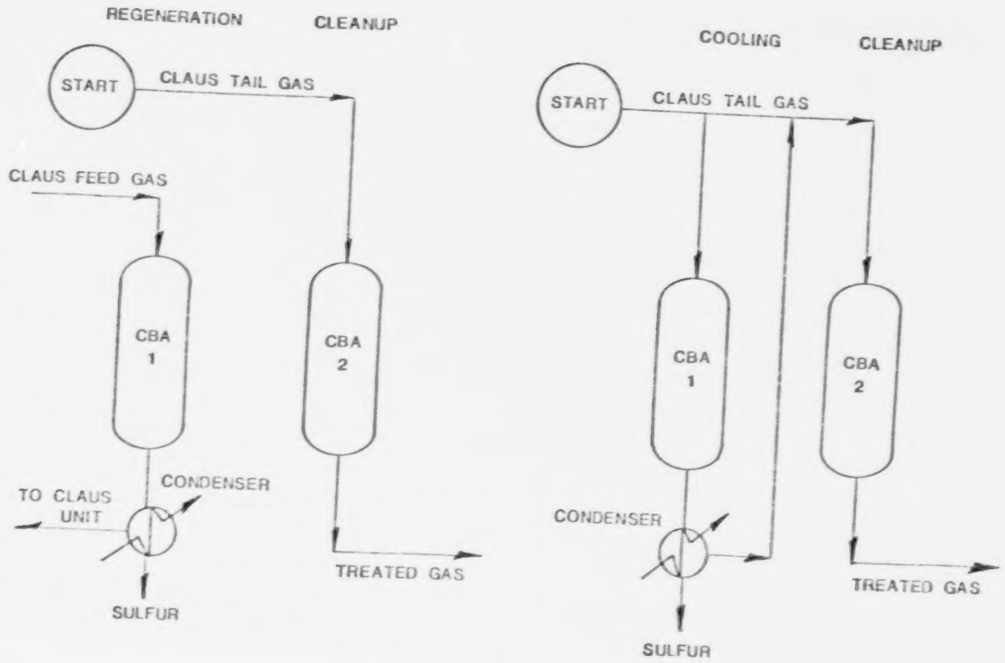

REGENERATION
CLEANUP
START
CLAUS TAIL GAS
CLAUS FEED GAS
CBA 1
CBA 2
TO CLAUS UNIT
CONDENSER
SULFUR
TREATED GAS
COOLING
CLEANUP
START
CLAUS TAIL GAS
CBA 1
CBA 2
CONDENSER
SULFUR
TREATED GAS

Figure E3-2. The CBA Process

a sulfur condenser. The hot gas is returned to the Claus cycle just downstream of the first Claus sulfur condenser. The flow diagram for a typical CBA unit is shown in Figure E3-2.

Construction and operation of a CBA unit are similar to those for a conventional Claus unit; energy consumption is low because no additional fuel is required. The process is suitable for retrofit installations because only a small plot area and minor modifications to the Claus unit are required.

Capital costs for adding a CBA unit to an existing Claus unit are estimated to be equal to the cost of the Claus unit. The CBA process is estimated to cost about half as much as a standard three-stage Claus unit, when installed at the same time as the Claus unit.

As of April 1979, there were three operational CBA units. Amoco claims an overall efficiency of 98 to 99 percent (Claus plus CBA). A 99 percent efficiency corresponds to about 1,500 ppmv SO_2 in the incinerated tail gas. Levels of COS and CS_2 are not reduced by the CBA process; therefore, formation of these compounds must be carefully minimized in the Claus unit.

The SNPA/Lurgi Sulfreen Process[17,22,23,24]--When the Sulfreen process was first introduced in 1968, six carbon beds in parallel were used to absorb the elemental sulfur formed in the Claus reaction and thus drive the reaction to completion. Later developments have led to the use of fewer standard Claus catalyst beds (alumina) with a lowered temperature as in the Amoco CBA process. Gas from the reactor is incinerated. The flow diagram of a typical Sulfreen unit is shown in Figure E3-3.

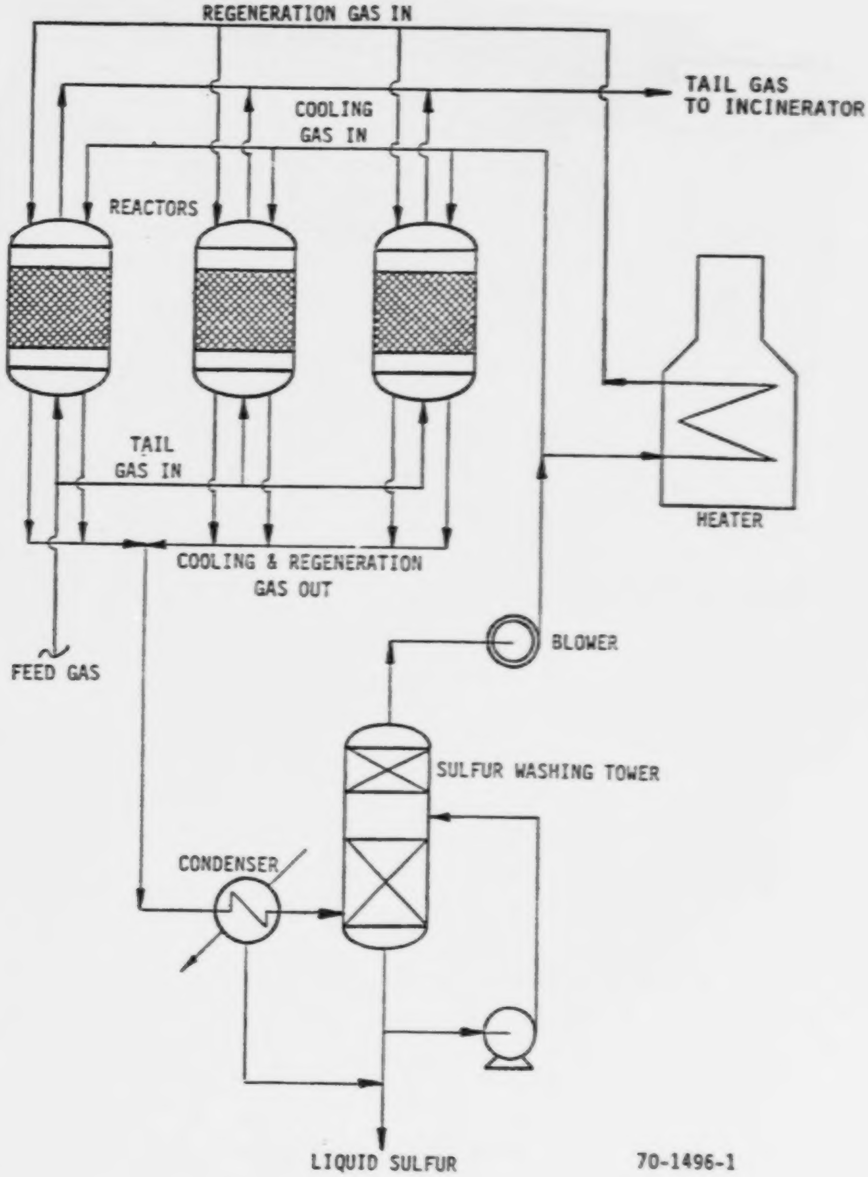

REGENERATION GAS IN
TAIL GAS TO INCINERATOR
COOLING GAS IN
REACTORS
HEATER
TAIL GAS IN
COOLING & REGENERATION GAS OUT
FEED GAS
BLOWER
SULFUR WASHING TOWER
CONDENSER
LIQUID SULFUR
70-1496-1

Figure E3-3. The SNPA/Lurgi Sulfreen Process

In the Sulfreen process, hot gas, mostly nitrogen, is blown through the beds to vaporize the sulfur and thus regenerate the bed. The sulfur is then collected in a sulfur condenser. The condensing sulfur generates 50 psig steam to be used elsewhere in the plant. Reactors are cooled with unheated gas before being returned to service. To provide more continuity, an improved flow scheme with three reactors is now being offered. Exchange of the reactor loop from one reactor to another is done automatically in 48-hour cycles.

Oxygen can cause a buildup of sulfates on the catalyst. These sulfates decrease the effectiveness of the catalyst. Because the regeneration gas in the Sulfreen process is in a closed loop, oxygen in the regeneration gas can be avoided and H_2S can be added to reduce a major portion of the sulfates formed during absorption. The ability to attack these sulfates and their formation is a principal characteristic of the Sulfreen process.

As of April 1979, there were 19 Sulfreen plants in operation and three under construction. They are located in France, Canada, and West Germany. The original Sulfreen plant, started up in 1970 and still using its original charge of carbon catalyst, removes 75 percent of the SO_2 from the Claus unit tail gas. The Claus unit itself has a 91 percent efficiency for an overall efficiency of 97.8 percent.

The effectiveness of a Sulfreen unit is dependent on the H_2S and SO_2 concentrations in the feed gas to the unit. At 15,000 ppmv H_2S and SO_2 in the feed gas, 85 percent conversion in the Sulfreen unit can be expected. This value drops to 70 percent for 8,000 ppmv H_2S and SO_2. For typical Claus-Sulfreen installations, an overall theoretical conversion of 99 percent is attainable with 2,500 ppmv H_2S and SO_2 in the treated tail gas and 1,500 ppmv or less SO_2 after incineration. COS and CS_2 levels are not affected by the Sulfreen process.

As in the case of the CBA process, construction and operation are similar to those for a conventional Claus unit. The facility is compact and can easily be retrofitted to an existing sulfur plant. Though the Sulfreen process uses fuel where the CBA process does not, it also produces more usable steam. Capital and operating costs for the Sulfreen process are comparable to those of the CBA process.

The Sulfreen process is attractive in large refineries when it can eliminate the need for a third or fourth Claus converter and reduce the required height and size of the tail gas disposal site. It is also attractive in smaller refineries where emissions of 1,500 - 2,000 ppmv SO_2 are allowable.

The Institut Francais du Petrole (IFP-1500) Process[17,23]--The IFP-1500 is a liquid phase continuation of the Claus reaction. It may be followed by an incineration unit. With this process, SO_2 emissions from a two-stage Claus plant can be reduced to 1,500 - 2,000 ppm. The process has no effect on COS or CS_2 emissions.

A schematic diagram of the basic IFP-1500 process is given in Figure E3-4. In the packed tower, a low vapor pressure polyethylene solvent which contains a proprietary carboxylic acid salt catalyst in solution circulates countercurrent to the incoming tail gas. The catalyst complexes with H_2S and SO_2 in an exothemic reaction; the complex then reacts with more H_2S and SO_2 to form elemental sulfur and to regenerate the catalyst. Heat is removed by injecting and vaporizing steam condensate to maintain a temperature of about 250 - 270°F. At this temperature, the sulfur is molten and

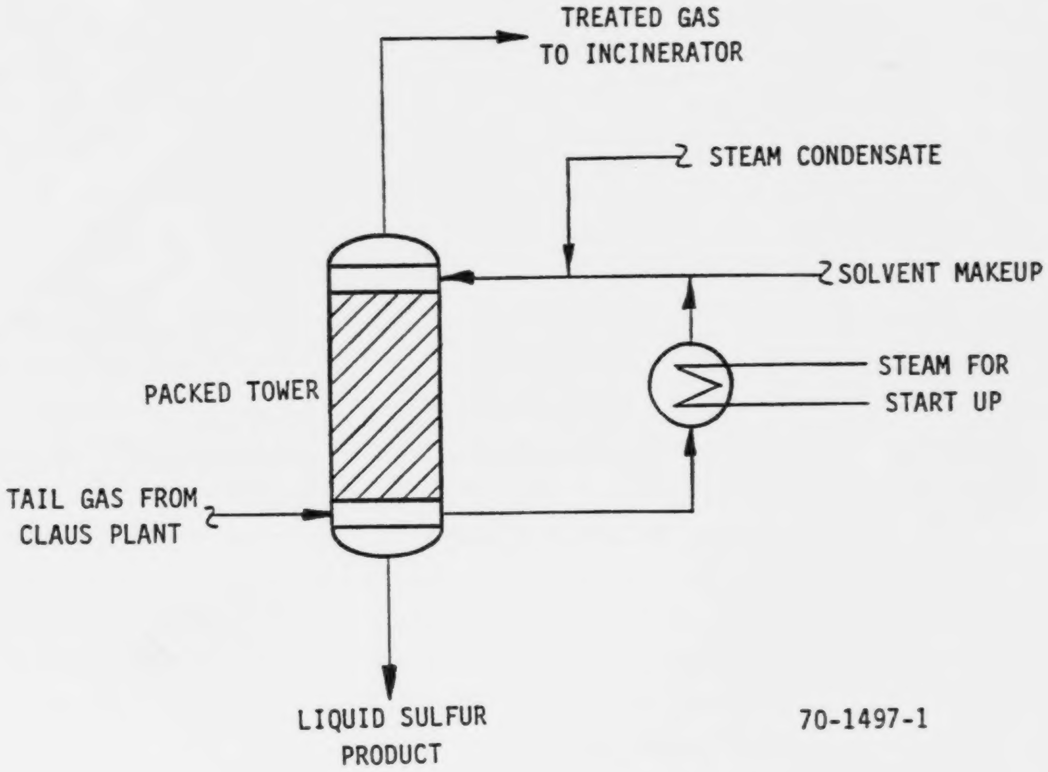

TREATED GAS
TO INCINERATOR
STEAM CONDENSATE
SOLVENT MAKEUP
STEAM FOR
START UP
PACKED TOWER
TAIL GAS FROM
CLAUS PLANT
LIQUID SULFUR
PRODUCT
70-1497-1

Figure E3-4. The IFP-1500 Process.

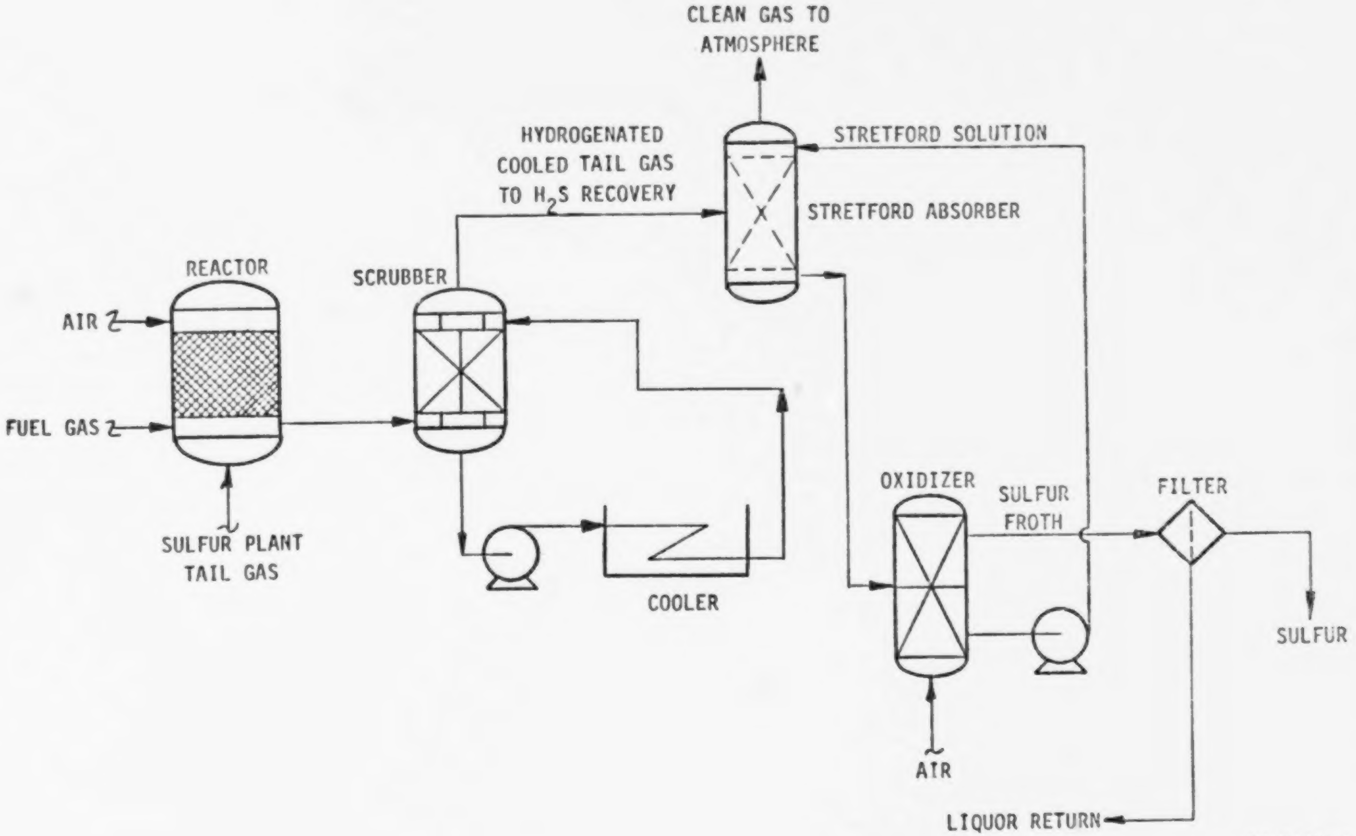
there is little loss of sulfur or glycol. Treated gas is incinerated, treated further or exhausted. Solvent is recirculated.

Corrosion is not a problem in IFP-1500 units because there is no water buildup. The entire unit can be made of carbon steel. The unit can also go as long as two years between shutdowns. After about two years, the unit is washed with water to flush out catalyst that has been converted to sulfates and has deposited on the packing in the tower. No extraordinary maintenance is required.

Because little plot area is required and there is no recycle of gas to the Claus unit feed, an IFP-1500 unit can easily be retrofitted to an existing Claus unit.

Of all Claus tail gas clean-up methods which can reduce SO_2 levels to 1,000 - 2,000 ppmv, the IFP-1500 process is probably the simplest in operation and design and requires the lowest capital investment. It can be economically adapted to even the smallest of Claus units. As of April 1979, there were 25 IFP-1500 units in operation, under construction, or being designed.

The Beavon Sulfur Removal Process[23,25,26]--The Beavon Sulfur Removal Process (BSRP) is one of the most commonly used designs for controlling the emissions from a Claus unit. Thirty-six BSRP units were in operation or under construction as of April 1979. In this process, the sulfur compounds in the tail gas are converted to H_2S and recovered as elemental sulfur by the Stretford process. The BSRP process is illustrated in Figure E3-5.


CLEAN GAS TO
ATMOSPHERE
HYDROGENATED
COOLED TAIL GAS
TO H_2S RECOVERY
STRETFORD SOLUTION
STRETFORD ABSORBER
REACTOR
SCRUBBER
AIR
FUEL GAS
SULFUR PLANT
TAIL GAS
COOLER
OXIDIZER
SULFUR
FROTH
FILTER
SULFUR
AIR
LIQUOR RETURN

70-1500-1

Figure E3-5. The BSRP Process.

The tail gas is reduced over a cobalt-molybdenum catalyst in a reducing gas atmosphere. Temperature and pressure are moderate. Sulfur plant tail gas usually contains more than enough hydrogen (about 2.5 percent) for hydrogenation. Sulfur dioxide and elemental sulfur are reduced to H_2S by the following reactions:

$$SO_2 + 3H_2 \rightarrow 2\ H_2O + H_2S \qquad (1)$$

$$S_2 + 2\ H_2 \rightarrow 2\ H_2S \qquad (2)$$

The catalyst also reacts water vapor with CO, COS, and CS_2 in the following hydrolysis reactions:

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad (3)$$

$$CS_2 + 2\ H_2O \rightarrow 2\ H_2S + CO_2 \qquad (4)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (5)$$

After hydrogenation and hydrolysis, the stream is cooled by water scrubbing. The vapor leaving the cooling unit contains about 2 - 4 percent H_2S, 12 percent CO_2, and the rest mainly nitrogen.

The H_2S-rich stream from the Beavon unit is then sent to the H_2S absorber column of the Stretford unit where it is contacted with the "Stretford Solution" of sodium carbonate and sodium vanadate. The H_2S is absorbed by the sodium carbonate and precipitated by the sodium vanadate:

$$H_2S + NA_2CO_3 \rightarrow NaHS + NaHCO_3 \qquad (6)$$

$$NaHS + NaHCO_3 + 2\ NaVO_3 \rightarrow S + Na_2V_2O_5 + Na_2CO_3 + H_2O \qquad (7)$$

Complexing agents such as sodium potassium tartrate or citric acid are sometimes used in the absorber to prevent deposition of vanadium in systems operating beyond their capacity; solubilized iron with Bellasol S.C.S. or EDTA may be used to speed up the reoxidation of some unwanted colored by-products.

The treated gas from the absorber is odorless and essentially free of COS and H_2S. Sulfur compounds, mainly COS, are generally equivalent to less than 100 ppm SO_2. No incineration of this stream is required during normal operation, but provisions must be made for upsets.[17]

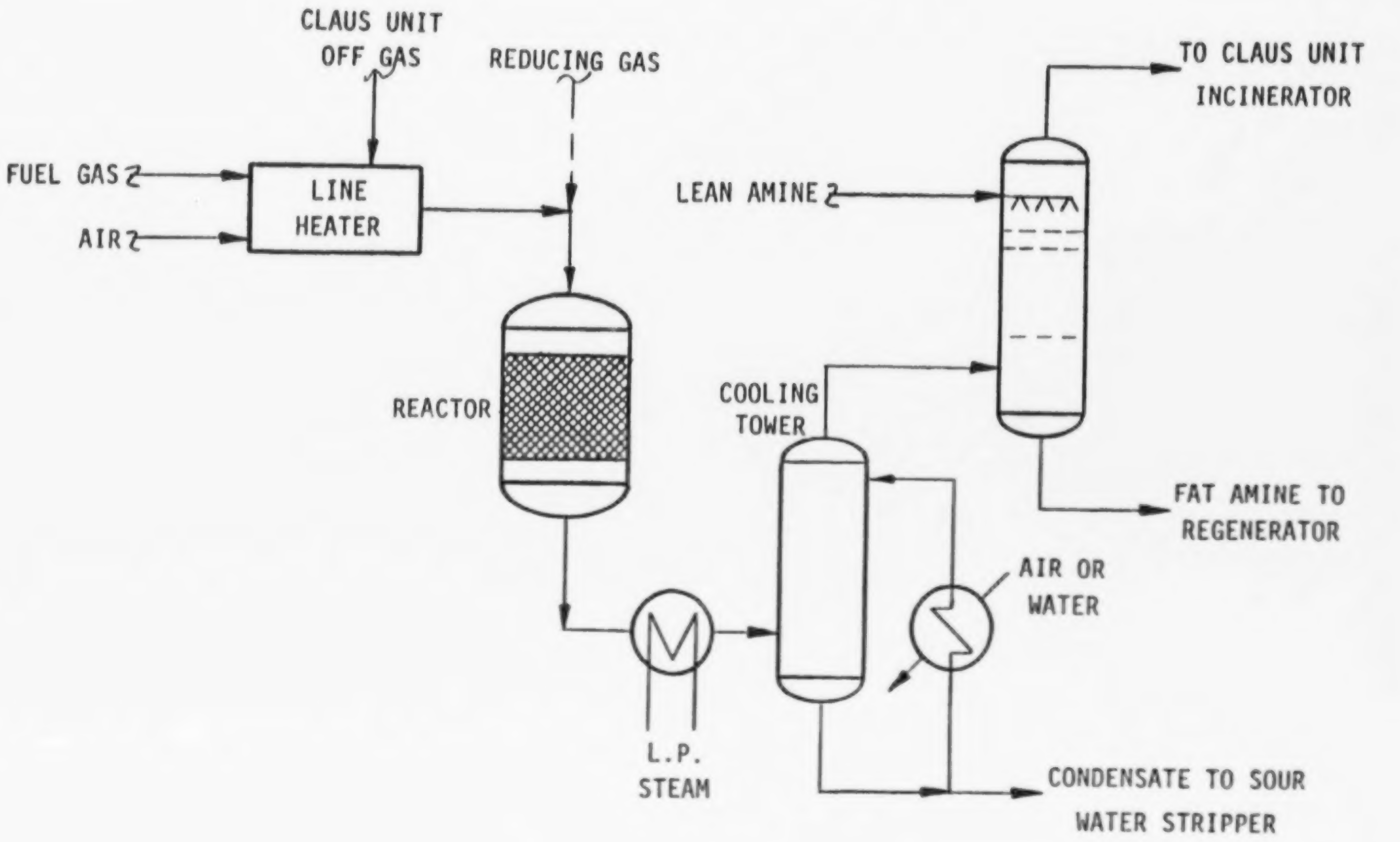
The liquor from the absorber is sent to an oxidizer where air is blown into the stream and the sodium vanadate is regenerated by sodium anthraquinone disulfonate (ADA):

$$Na_2V_2O_5 + \frac{1}{2} O_2 \xrightarrow{ADA} 2\ NaVO_3 \qquad (8)$$

The finely divided sulfur forms a heavy froth which is skimmed off, filtered, and washed. Reoxidized solution is pumped to the absorber.

The total investment for a BSRP unit is approximately equal to that of the parent Claus unit. Normally, the BSRP process should be considered for larger (≥100 lt/day) Claus plants. If adequate space is available, the process is suitable for retrofitting since no streams are recycled to the Claus unit.

The Shell Claus Off-Gas Treating (SCOT) Process[6,17,23,27]--The SCOT process, like the BSRP, entails the reduction of all sulfur compounds in the Claus unit tail gas to H_2S. It is shown in Figure E3-6. In a manner similar to that of the


CLAUS UNIT
OFF GAS
REDUCING GAS
TO CLAUS UNIT
INCINERATOR
FUEL GAS
AIR
LINE
HEATER
LEAN AMINE
REACTOR
COOLING
TOWER
FAT AMINE TO
REGENERATOR
AIR OR
WATER
L.P.
STEAM
CONDENSATE TO SOUR
WATER STRIPPER

70-1501-1

Figure E3-6. The SCOT Process

BSRP, the tail gas, along with a reducing gas, is passed over a cobalt-molybdenum catalyst. Sulfur dioxide, elemental sulfur, COS and CS_2 are converted to H_2S according to reactions (1), (2), (3), and (4) of the section "The Beavon Sulfur Removal Process." The gas which leaves the reactor is cooled, and the water is condensed.

The cooled gas, which normally contains up to 3 volume percent H_2S and up to 20 volume percent CO_2, is then scrubbed with an alkanolamine solution in an absorption column. The absorber is designed so that H_2S is almost completely absorbed while relatively little (30 percent) of the CO_2 present in the absorber feed gas is absorbed. The overhead stream from the absorber, which contains 200 - 500 ppmv H_2S, is routed to the Claus incinerator.

The rich amine solution from the absorber is then steam-stripped to release H_2S and CO_2; steam is removed by condensation. The top gas containing the H_2S and CO_2 is recycled to the front end of the Claus unit.

Because of the recycle of CO_2, the SCOT process is not suitable for streams rich in CO_2 and low in H_2S. It is also sensitive to the H_2S/SO_2 ratio in the Claus unit tail gas. It is, however, considered one of the most flexible processes available for Claus tail gas cleanup with respect to turndown capability. It can be operated at from 20 - 100 percent of design feed ratio.

Nearly all mechanical equipment for a SCOT unit can be fabricated of carbon steel. Minimum pressure drop can be designed into the system to facilitate ultra-filtering. If a

SCOT unit is retrofitted, the cost is about equal to that of the parent Claus unit. A SCOT unit can be incorporated into a new facility for about 75 - 80 percent of the cost of the Claus unit.

As of April 1979, there were more than 35 SCOT units in operation in the United States and Canada. More than 25 others were in design, construction, or commissioning around the world. Claus units using SCOT units were as large as 2,100 lt/day and as small as 3 lt/day.

The Wellman-Lord (W-L) Process[17,23,27,28]--The Wellman-Lord process is applied to the cooled fuel gas from the Claus plant incinerator. It can also be used to desulfurize a number of other types of flue gases. This process is illustrated in Figure E3-7.

In the Wellman-Lord process, the SO_2-rich gas is contacted with a sodium sulfite solution in an absorber. Sodium bisulfite is formed according to the following reaction:

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2\ NaHSO_3 \qquad (1)$$

Some sodium bisulfite is oxidized to sodium sulfate:

$$Na_2SO_3 + \frac{1}{2}\ O_2 \rightarrow Na_2SO_4 \qquad (2)$$

Desulfurized flue gas (about 200 ppmv SO_2 or less) is released to the atmosphere. The absorber solution is fed to an evaporator where SO_2 and steam are evaporated. The SO_2 can be fed to the Claus plant or to a sulfuric acid plant.

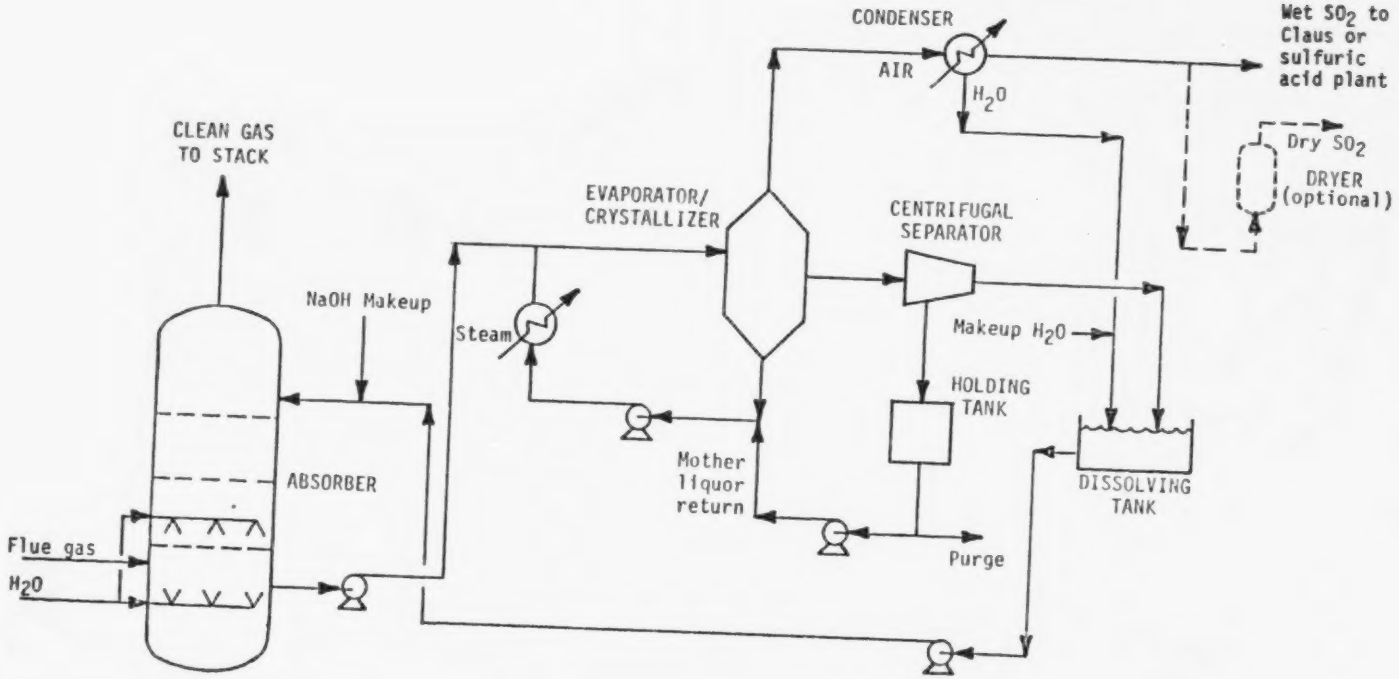

CONDENSER
AIR
H_2O
Wet SO_2 to Claus or sulfuric acid plant
Dry SO_2
DRYER (optional)
CLEAN GAS TO STACK
EVAPORATOR/ CRYSTALLIZER
CENTRIFUGAL SEPARATOR
NaOH Makeup
Steam
Makeup H_2O
HOLDING TANK
Mother liquor return
ABSORBER
DISSOLVING TANK
Flue gas
H_2O
Purge

Figure E3-7. The Wellman-Lord Process.

About 15 percent of the effluent from the evaporator is routed to a purge treatment area where a mixture of sodium sulfite and sodium sulfate is crystallized out of solution. The sodium sulfate/sodium sulfite crystals are dried for sale or disposal. Sodium lost during the purge operation is replenished by the addition of sodium hydroxide to the regenerated liquor.

Sodium loss through sulfate formation is a major concern. This loss can be minimized by maintaining a high sulfite concentration in the absorber. In one installation, a proprietary chemical has been added to the absorber to halve sodium loss. Fractional crystallization of the purge steam can increase the sulfate content of the purged solids to 70 percent.

Because the Wellman-Lord process treats the tail gas after incineration, the H_2S/SO_2 ratio from the Claus unit is not critical. Streams high in CO_2 are well suited to the process because CO_2 is not recycled.

Cost of a Wellman-Lord unit is high, however, partly because of the corrosion-resistant metals required. For a 100 lt/day Claus plant, a Wellman-Lord unit would cost about 130 - 150 percent of the cost of the parent Claus unit. Cost penalties are particularly severe for smaller installations; the Wellman-Lord process probably should not be considered for Claus plants 50 lt/day or smaller.

As of April 1979, there were seven Wellman-Lord units being used for Claus tail gas cleanup in the United States and Japan. Nineteen others were treating other sulfur-bearing flue gases.

Costs--The actual costs of sulfur recovery processes are very sensitive to the flow rate and composition of the input gas stream. Some processes are available in capacities ranging from skid-mounted units to full scale process units. Most of the cost information available in the literature is three or four years old. Changes in process technology have probably changed these costs to a greater extent than the effects of overall process cost escalations and some costs may have decreased. Factors other than costs or energy requirements may be responsible for the selection of the appropriate process for a particular installation.

3.2.1.4 Catalyst Regeneration

FCCU Catalyst Regeneration--Regeneration of the catalyst in fluid catalytic cracking units (FCCU's) produces three principal types of atmospheric emissions: SO_x particulates, and CO. Lesser emissions include hydrocarbons, NO_x, aldehydes, and ammonia. SO_x is typically controlled by feedstock dedulfurization; particulates by cyclones and electrostatic precipitators; and CO by a CO boiler. No single process can control all three.

SO_x Emissions - Hydrodesulfurization (HDS) of feed stock to FCCU's has been practiced for years, since it increases the yield of salable products. In HDS of FCCU feedstock, the ratio of weight percent sulfur in the coke over the weight percent sulfur in the desulfurized feedstocks increases with the degree of desulfurization. The result is that very high levels of hydrodesulfurization are needed to achieve 90 percent of higher reduction of SO_x emissions. For a feedstock with 2.3 weight percent sulfur, 92 - 95 percent desulfurization of the feed is necessary for a 250 ppm SO_x concentration in the flue gas.[29] A more complete description of HDS processes is given in Section 4.4 of Appendix F.

Particulates (catalyst fines) - Before exiting the regenerator, gases pass through a series of cyclones that remove the small catalyst particles (fines) present in the exit gas. Some refineries have additional cyclones downstream of the regenerator.

Particles smaller than 5 microns are ordinarily not collected by cyclones. The majority of refineries use electrostatic precipitation to remove these catalyst fines from the flue gas. Cyclones and electrostatic precipitators are discussed in Section 3.2.1.1 under the headings "Cyclones" and "Electrostatic Precipitators."

The collecting efficienty of ESP's for catalyst fines is commonly 90 - 99 percent of the particles that escape the cyclones. In most cases, final disposal of the waste particles is by burial in a sanitary landfill.

CO Emissions - All methods of controlling the CO content of flue gas from FCC regeneration involve combustion of CO to CO_2. A typical unit with "conventional" regeneration burns off the coke from spent catalyst to, roughly, a 50 - 50 mixture of CO and CO_2.

The majority of refineries--66 percent in 1976--used a CO boiler to recover part of the energy from hot FCCU flue gases and to reduce CO emissions.[30] The flue gas goes to the furnace of a CO boiler and external heat is applied to raise the temperature high enough (~1,300°F) to achieve near complete combustion (99.5 percent or more). The heat of combustion is recovered as steam, often used to drive the regenerator air blower as well as for other refinery operations.

In all but small refineries, the cost of CO boilers can be recovered in a few years. Small refineries may find it more economical to control CO emissions with flares, even though no energy recovery is possible.

Other Catalyst Regeneration--Because emissions from TCCU catalyst regeneration are significantly less than those from FCCU catalyst regeneration, use of a CO boiler may not be justified. Flue gases from TCC catalyst regenerators are usually released directly to the atmosphere.

Flue gases from other catalyst regenerators may also be incinerated in a process heater or flared, but use of these control methods is not widespread because these emission sources are small.

3.2.1.5 Boilers and Process Heaters

No pollution control devices for refining boilers and process heaters are in current use.[31] Combustion modification is discussed in Section 4. When low emissions are required, only clean fuels are burned and high-efficiency burners are used. It should be recognized that these boilers and process heaters themselves can act as control devices when they are used to incinerate waste process streams.

3.2.1.6 Vacuum Distillation[10]

Emissions of noncondensable vapors from vacuum distillation are controlled by venting into a blowdown system or by incineration. The vapors may be used as supplemental fuel in process heaters and boilers. Oily condensate emissions can be eliminated by the use of mechanical vacuum pumps or surface condensers which discharge to a closed drainage system. Both noncondensable and condensable emissions can be minimized by the installation of a lean-oil absorption unit between the vacuum tower and the first stage vacuum jet.

These control methods virtually eliminate process emissions from vacuum distillation.

3.2.1.7 Coking

Particulate emissions from the delayed coking process can be minimized by wetting down the coke during the coke removal procedure. Hydrocarbon emissions can be minimized by venting the quenching steam to a vapor recovery or blowdown system. Once the drum has cooled to 212°F, the steam purge can be replaced by a water flood. Further cooling to approximately ambient temperatures will minimize steam and hydrocarbon vaporization when the drum is opened.

Cooling to ambient temperatures and using large amounts of water to reduce emissions from delayed coking units are not practical in many instances. Cooling the coke to ambient temperatures before removing it from the drum increases the chance that the coke can "set up." If it sets up, removal may be possible only by tedious, time consuming methods. Excess water on the coke once it has been removed produces a water pollution problem, could produce an off-specification green coke, could plug coke handling systems in the calciner feed section, and would upset calciner operations at those installations producing premium calcined coke.

Significant particulate emissions often occur during the loading of calcined coke into rail cars or trucks. An induced draft particulate control system using bag filters could reduce these emissions, but would be expensive to design, install, and maintain. A more reasonable approach is to spray the combined coke with a small amount of oil (heavy cycle oil or coker gas oil) as it leaves the cooler.

Fluid coking units can emit particulates and carbon monoxide. The off-gas from the coker can be controlled by incineration in process heaters or CO boilers. In some cases, the CO boiler used is the same one that controls CO emissions from the fluid catalytic cracking unit. Particulate emissions from the CO boiler are controlled by the methods described in Section 3.2.1.4.

3.2.1.8 Air Blowing

In many refineries, air-blown brightening units have been replaced with packed vessels containing solid adsorbents.[10] These units have slight potential for process hydrocarbon emissions.

Emissions from asphalt blowing can be reduced by vapor scrubbing, incineration, or a combination of both. Vapor scrubbers condense steam, aerosols, and essentially all of the hydrocarbon vapors. A disadvantage in water scrubbing is the high-volume ratio of water-to-exhaust gas required to remove the hydrocarbons. When an adequate water supply is not available or when condensate handling may result in hydrocarbon emissions, incineration of the vapors by direct flame contact may be used. Incineration may be accomplished in process heaters, boilers, or flares.

Hydrocarbon emissions from a controlled asphalt-blowing unit are negligible.[32]

3.2.1.9 Chemical Sweetening

Emissions from the inert gas stripping of spent caustic can be prevented by venting the gases to a flare or a furnace firebox.

Emissions from air blowing regeneration of spent oxidative sweetening solutions can be reduced by steam-stripping the spent solutions to recover hydrocarbons before air-blowing. The gaseous effluent from air blowing can be incinerated to dispose of residual hydrocarbons.

3.2.1.10 Acid Treating

If the acid concentration process is used, the off-gases from the mist eliminator can be vented to caustic scrubbers for SO_2 and odorant removal, and then to an incinerator or a flare.

Hydrocarbons escaping from acid recovery operations can be eliminated by using acid regeneration. Regeneration involves sludge incineration to produce SO_2, which can be converted to H_2SO_4. Some of the SO_2 control methods discussed in Section 3.2.2 are available for control of SO_2 emissions from acid sludge incineration.

3.2.1.11 Blowdown

Blowdown emissions can be effectively controlled by venting into an integrated vapor-liquid recovery system. All units and equipment subject to shutdown, upsets, emergency venting and purging are manifolded into a multi-pressure collection system. Discharges into the collection system are segregated according to their operating pressures. A series of flash drums and condensers arranged in descending operating pressures separate the blowdown into vapor pressure cuts. The liquid cuts are recycled to the refinery; the gaseous cuts are recycled or flared.

Emissions from a controlled blowdown system have been estimated to be 0.8 lb per thousand barrels of refinery feed; compared to 580 lb per thousand barrels for uncontrolled. The control is estimated to be 99.9 percent effective.[5]

3.2.1.12 Compressor Engines

No pollution control devices for refinery compressor engines are in current use.[5] Combustion modification is discussed in Section 4.

3.2.2 Control Technology Available in Refineries

Controls with limited application and those which have not yet been applied are included in this section. Information available on new technologies is often limited.

The methods chosen for inclusion in this section are those which have been proposed for consideration by the industry. Inclusion of a method here indicates only that it is worthy of consideration, not that it is necessarily a good choice for any particular application.

3.2.2.1 Particulate Control for Incinerators

Filters--There are many kinds and several types of filters that may be used for particle removal. The types of filters include flexible sheets, tubes, or bags of porous material; supported semirigid fabrics or nonwoven fibrous mats; and fixed or fluidized beds of dry granules or particles.

The filters used to make fabric or mat filters may be wool, cotton, dacron or other synthetics, asbestos, fiberglass, or metal. These materials may be used in their natural state or they may be treated to give them an electrostatic charge or to make them adhesive. Fixed or moving beds may be composed of ceramic, sand, coke, crushed rock, or other materials.

Filters can often remove more than 90 percent of the particles on micron or larger in size. But fabric filters are not generally used for gases containing more than 10 to 12 grans per cubic foot. They also cannot be used if there is any kind of condensate in the gas stream.

It is not usually necessary to have a filter with a high initial efficiency because the efficiency increases as particles collect on the filter. There is an accompanying increase in the pressure drop, however, and the filter is cleaned or replaced when this pressure drop becomes unacceptable.

Wet Collectors--Wet collectors are divided into two categories according to the particle size they collect most efficiently. Those which collect particles down to one micron in size include spray towers, centrifugal spray scrubbers, and self-induced spray scrubbers. Disintegrator scrubbers, venturi scrubbers, and foam scrubbers collect particles less than one micron in size.

In spray towers, droplets are formed by atomizing sprays and are collected by gravity. These droplets in a centrifugal spray scrubber are also formed by an atomizing spray, but are collected by centrifugal force. In a self-induced spray scrubber, gas breaks up the liquid into droplets.

To form droplets in a disintegrator scrubber, liquid is sheared as it passes between a rotor and a stator. The liquid is dispersed by high velocity gas in the venturi scrubber. Sieve trays produce foam in foam scrubbers.

Wet collectors may be used on gas streams where addition of liquid to the gas streams is not objectionable. The gas is cooled and vapors or gaseous contaminants removed. Particles with diameters ranging down to 0.5 micron are collected with a moderately high efficiency. Particles less than 0.5 micron are collected at a lower efficiency.

When wet collectors are used, there is a reduced danger of explosion, but there is an added potential for corrosion and freezing. Disposal of the sludge is also a problem.

Wet collectors are not usually advised when a less expensive device, such as a cyclone or a centrifugal separator will be satisfactory. Wet collectors are about as costly as filters such as cloth bags, but are preferable to filters because they are less affected by high temperatures and high loads. Their efficiency is not generally as good as that of a filter, however.

3.2.2.2 Sulfur Recovery

The control of emissions from the Claus unit is a subject of great concern in the refining industry. A number of control methods have been proposed in recent years. Some are applicable only to Claus tail gas while others may be applied to other sulfur-bearing streams as well. Also being tested are an alternate to the Claus unit and a modification of the unit. The alternate would produce no objectionable tail gas stream.

Most of the tail gas treatment methods included in this section are described briefly in Table E3-11.

TABLE E3-11. AVAILABLE METHODS FOR REMOVAL OF SULFUR FROM CLAUS TAIL GAS

Name	Developer	Description	Efficiency or Outlet Concentration (Claus + Addition)	Product	Cost (% Cost of Claus)
IFP-150	Institut Francais du Petrole	Gas from IFP-1500 scrubbed with ammonia; SO_2- laden ammonia mixed with H_2S in a glycol to form elemental sulfur and water.	<200 ppm SO_2	S_o	variable
Clean air	Pritchard	Claus reactors operated at high temperature to reduce COS & CS_2 levels; SO_2 + elemental sulfur removed by aqueous scrubbing; H_2S removed by Stretford process.	50 ppmv SO_2	S_o	100%
Trencor-M	Trentham	All sulfur compounds reduced to H_2S. H_2S absorbed by amine solution & returned to Claus.	100-200 ppmv SO_2	feed to Claus	150%
Aqua Claus	Stauffer	SO_2 from incineration mixed with H_2S-rich Claus feed; Claus reaction occurs in aqueous phase.	<100 ppmv SO_2	S_o Na_2SO_4	125-135%
Sulfoxide	Alberta Sulfur Research, Ltd.	Claus reaction occurs in an organic sulfoxide medium	<1000 ppmv S typically <500 ppmv S	S_o	Not available
Topsoe	SNPA/Topsoe	SO_2 from incineration oxidized to SO_3 which is converted to H_2SO_4.	97%	H_2SO_4	Not available
SFGD	Shell	SO_2 in gas from incineration absorbed by CUO bed which is regenerated with hydrogen.	97%	Feed to Claus	250%

Continued

TABLE E3-11. (Continued)

Name	Developer	Description	Efficiency or Outlet Concentration (Claus + Addition)	Product	Cost (% Cost of Claus)
Westvaco	Westvaco	SO_2 in gas from incineration removed and catalyzed to H_2SO_4 in activated carbon bed which is regenerated with H_2S.	<200 ppmv SO_2	S_o or feed to Claus	Not available
Ammonium Bisulfate/ Ammonium Thiosulfate	Pritchard	SO_2 in gas from incineration absorbed in aqueous ammonia & converted to ammonium thiosulfate.	<900 ppmv SO_2	Ammonium thiosulfate	75%
BSR/ Selectox I	Union Oil	All sulfur compounds reduced to H_2S which is then oxidized to S_o.	>98%	S_o	$\leq$200%
Limestone Slurry	Mineral & Chemical Resource Co.	SO_2 in incinerator gas absorbed by limestone slurry.	>99.9%	$CaSO_3/CaSO_4$ limestone solid	Not available
Catalytic Incineration	Institut Francais du Petrole	Catalyst promotes oxidation of sulfur compounds to SO_2 in incinerator.	<200 ppmv S	SO_2	Not available

The UOP Sulfox Process[33]--The UOP Sulfox process is an alternative to the Claus process. In this process, aqueous ammonia, instead of an amine solution, is used to scrub H_2S from refinery streams. Ammonia is then scrubbed from the gas with purified water.

The rich solution is mixed with air and sour water and passed over a catalyst. Elemental sulfur is formed according to the following reaction:

$$NH_4HS + \frac{1}{2} O_2 \rightarrow S_0 + H_2O + NH_3 \qquad (1)$$

With ammonia and sulfide present, the elemental sulfur remains in solution as polysulfide. The liquid product from this reaction is then heated above the melting point of sulfur, mixed with air, and passed over a second catalyst bed where any remaining sulfide is oxidized to elemental sulfur. With no sulfide remaining to solubilize the sulfur as polysulfide, the sulfur exists as a separate molten product.

In each reactor, some sulfide is oxidized to thiosulfate. A minor portion of the thiosulfate is then oxidized to sulfate. The operating conditions and the catalyst are chosen to minimize sulfate formation; any sulfate formed (0.1 to 0.5 percent of the sulfur) is discarded as ammonium sulfate.

Ammonia from the reactors can be recovered and reused as absorbent, or it can be incinerated to nitrogen and water vapor. Ammonia in the original feed can be recovered as a product by distillation from a slip-stream of the sulfide-free effluent from the oxidizer.

Most of the effluent from the final oxidizer is used directly as absorbent solution. The remainder is carried to a reducer where the thiosulfate is reduced to sulfur by reaction with a portion of sulfide-rich solution which bypasses the oxidizer. This reaction is noncatalytic.

The tail gas from the oxidizers is scrubbed free of ammonia with water. Hydrogen sulfide content in the treated gas is 10 to 100 ppm. It is possible, at increased cost, to design a Sulfox unit which can achieve 1 ppm H_2S in the tail gas. However, NSPS requires less than 250 ppmv SO_2 from a final oxidizing step, which in this case would probably be interpreted as, "SO_2 or its equivalent as reduced sulfur compounds."

It may be possible to convert an existing Claus system to a Sulfox System with a minimum of expense. It is probable that the existing amine absorber could be used as the ammonia absorber and that the existing amine stripper could be used in the Sulfox unit proper.

Cost of a Sulfox system is considered about equal to that of a Claus unit, not including the cost of tail gas cleaning. Utility costs are estimated to be about 60 percent of those of a Claus unit.

The Mineral and Chemical Resource Company (MCRC)[33]-- The MCRC Sulfur Recovery process is actually a modified improvement of the Claus process. A proprietary scrubber is used to improve sulfur recovery and also to remove any ammonium sulfate which forms in a Claus unit if the feed contains ammonia.

The feed stream flows first into a special reaction furnace where a carefully controlled quantity of air oxidizes a portion of the H_2S to SO_2. The standard Claus reactions then occur. The hot gas from the furnace flows through a waste heat boiler to a condenser where elemental sulfur is condensed and withdrawn. The remaining gas flows to a converter where additional reaction takes place and then to another condenser for further sulfur removal. It may pass through several more converters and condensers until the desired sulfur removal is accomplished.

A 98 percent sulfur recovery efficiency can be obtained with a three converter design; greater than 99 percent efficiency can be obtained with four converters. Two MCRC sulfur recovery plants have been operating since 1976.

The Institut Francais Du Petrole (IFP-150) Process[34]--To increase the effectiveness of the IFP-1500 process, it can be coupled to an ammonia scrubbing section and then an IFP-150 unit. Ammonia scrubbing can reduce the sulfur dioxide content in the tail gas to below 200 ppm. The IFP section converts the ammonia scrubber liquor, mostly ammonium sulfites, to elemental sulfur and ammonia. The ammonia is recycled to the scrubber.

The liquor from the ammonia scrubber is first heated in a forced-circulation evaporator where sulfites are decomposed to ammonia and sulfur dioxide. Sulfates and thiosulfates in the liquor are reduced to ammonia, sulfur dioxide and water with a proprietary IFP process.

The ammonia-sulfur dioxide stream and hydrogen sulfide-rich gas are then fed to the IFP reactor at a 2:1 ratio of hydrogen sulfide to sulfur dioxide. In the reactor the hydrogen sulfide and sulfur dioxide dissolve in a high-boiling-point glycol to form elemental sulfur and water. The reaction temperature is maintained slightly above the melting point of sulfur and liquid sulfur is drawn off.

The IFP-150 process can be used for various other flue gases and acid or sour streams in a refinery to maintain SO_2 emission rate of less than 200 ppm at the stack mouth. Scrubbers can be set up at many points and their effluents piped to a central IFP-150 reaction section. Total sulfur recovery using the IFP-150 process in a refinery is shown in Figure E3-8.

The Pritchard Cleanair Process[26,33]--The Cleanair process is similar to the BSRP in that final cleanup is in a Stretford unit. A Cleanair unit can recover 99 percent of the sulfur in the Claus tail gas, leaving no more than 50 ppmv SO_2 equivalent in the effluent.

The first step in the Cleanair process is the reduction of COS and CS_2 levels by operating the Claus reactors at elevated temperatures. Sulfur dioxide and elemental sulfur are then removed from the tail gas by aqueous scrubbing. A Stretford unit then removes the hydrogen sulfide.

The plant cost for a Cleanair unit is roughly equivalent to that of a Claus unit and reauires about the same amount of space. Per daily ton of sulfur produced in the Claus tail gas, 4 kwh per hour, 8 lb steam per hour, 9 gpm water for cooling, and \$2.40 to \$3.00 per day for chemicals are required.

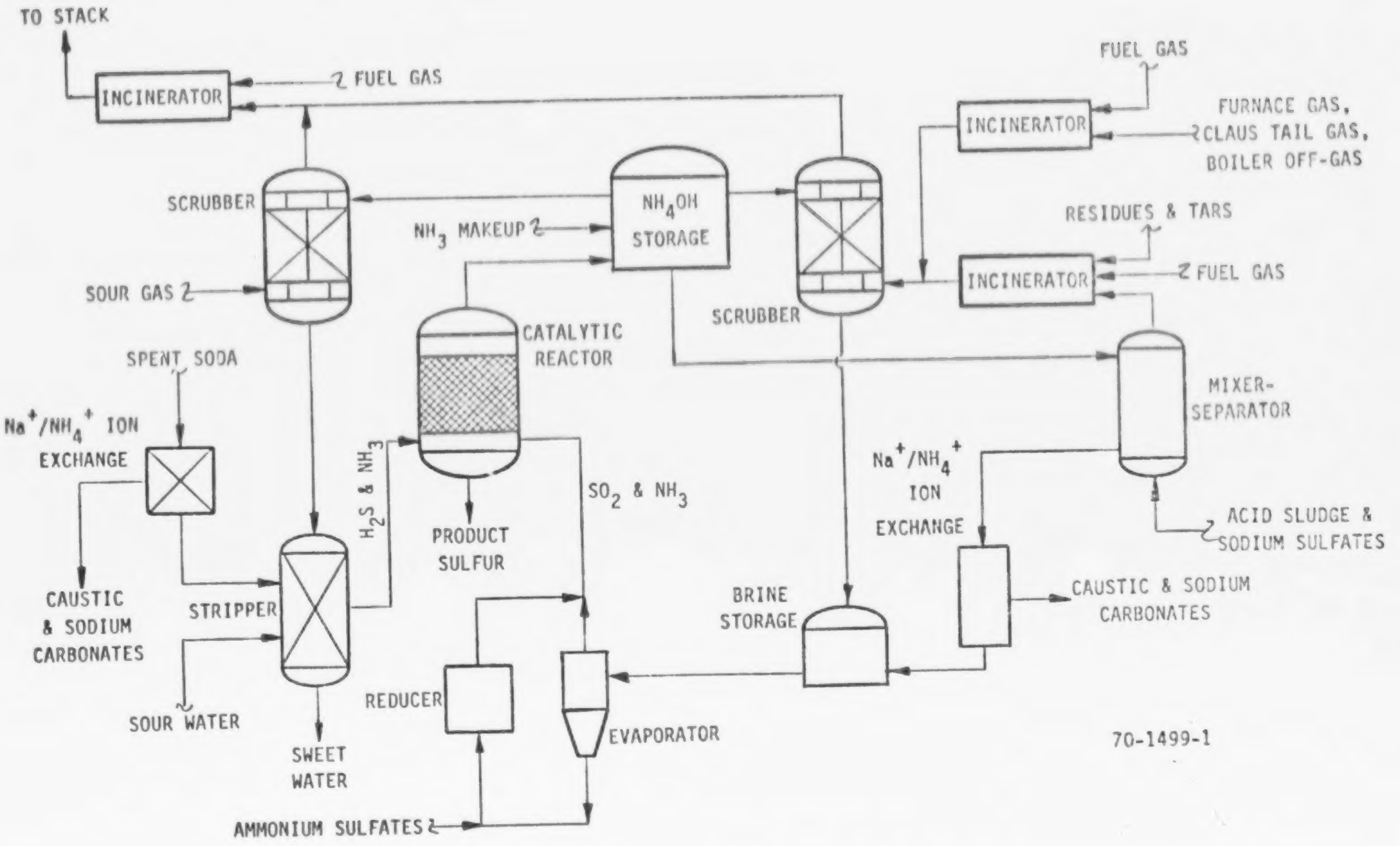

TO STACK
INCINERATOR
FUEL GAS
SCRUBBER
SOUR GAS
NH_3 MAKEUP
NH_4OH STORAGE
SCRUBBER
FUEL GAS
INCINERATOR
FURNACE GAS, CLAUS TAIL GAS, BOILER OFF-GAS
RESIDUES & TARS
INCINERATOR
FUEL GAS
CATALYTIC REACTOR
SPENT SODA
Na^+/NH_4^+ ION EXCHANGE
H_2S & NH_3
PRODUCT SULFUR
SO_2 & NH_3
MIXER-SEPARATOR
Na^+/NH_4^+ ION EXCHANGE
ACID SLUDGE & SODIUM SULFATES
CAUSTIC & SODIUM CARBONATES
STRIPPER
SOUR WATER
SWEET WATER
REDUCER
EVAPORATOR
BRINE STORAGE
CAUSTIC & SODIUM CARBONATES
AMMONIUM SULFATES
70-1499-1

Figure E3-8. Total Sulfur Recovery with the IFP-150 Process.

As of April 1979, there was one Cleanair unit providing a guaranteed 300 ppmv sulfur dioxide equivalent. Two other plants were under construction.

The Trentham Trencor-M Processor[27]--The Trencor-M process is similar to the SCOT process. All sulfur species in the tail gas are converted to H_2S over a cobalt-molybdenum catalyst. A proprietary aqueous solution of methyldiethanolamine (MDEA) with small amounts of inorganic salts absorbs the H S from the stream. The vent gas is incinerated. When the amine solution is regenerated, the H_2S-rich stream is recycled to the front of the Claus plant.

The Trencor-M process can reduce SO_2 levels to 100 - 200 ppmv. The investment cost is estimated to be 159 percent that of the parent Claus plant. As of mid-1978, there was one known commercial Trencor-M plant.

The Stauffer Aquaclaus Process[22,35]--The Aquaclaus process treats the Claus tail gas after it has been incinerated. The stream from the incinerator is first cooled in a waste-heat boiler and/or a direct-contact cooler. The SO_2 is then absorbed from the solution by the Aquaclaus solution (aqueous sodium phosphate) in an absorption tower. Off-gas from the absorber can contain less than 50 ppmv SO_2.

The SO_2-rich absorbent from the tower is then mixed with H_2S feed from the front of the Claus unit. Elemental sulfur is formed by the Claus reaction in aqueous phase. Liquid sulfur is withdrawn; the Aquaclaus solution is returned to the absorber.

The SO_2-rich absorbent from the tower is then mixed with H_2S feed from the front of the Claus unit. Elemental sulfur is formed by the Claus reaction in aqueous phase. Liquid sulfur is withdrawn; the Aquaclaus solution is returned to the absorber.

A purge stream is required for control of the levels of undesirable polythionates, thiosulfates and sulfates formed in the absorber and the Claus reactor.

An Aquaclaus plant which would recover 20-25 lb/d sulfur would cost about 125-135 percent of the cost of the parent Claus plant. As of mid-1978, there were no commercial installations of the process although it had been thoroughly tested in pilot plant operations.

The Aquaclaus process, like the IFP-150, has also been designed for total SO_x control in a refinery. Besides its use for cleanup of Claus unit tail gas, it can also be used for the tail gases from sludge acid regeneration, the CO boiler, and boilers and process heaters, as well as any other sulfur-bearing gas streams in the refinery. The process is not sensitive to contaminants or to operational upsets.

It is supposedly possible to use the Aquaclaus process in lieu of the Claus in a refinery. For this application, vacuum pitch is burned in the heaters and the SO_2 removed from the flue gases in phosphate absorbers. In a central facility, the phosphate solution is regenerated by the H_2S-rich streams from the hydrodesulfurization units. The vent gas from the regeneration is sent to the amine unit. The H_2S in the amine unit is then incinerated, and SO_2 in the incinerator off-gas removed in another phosphate absorber. The SO_2-rich gas is then sent to the central regeneration facility.

The Alberta Sulfur Research Ltd. (ASR) Sulfoxide Process[27]--In the Sulfoxide process, the Claus reaction occurs in an organic sulfoxide medium. The sulfoxide acts as a catalyst: the H_2S and the sulfoxide form an adduct which in turn complexes with other sulfur compounds.

Low concentrations of H_2S and SO_2 in the Claus tail gas can be almost completely converted to sulfur. More than 70 percent of the COS and CS_2 present can be converted to sulfur. The treated gas stream contains appreciably less than 1,000 ppmv sulfur, typically less than 500 ppmv sulfur, when the feed stream contains more than 30,000 ppmv sulfur compounds.

The Sulfoxide process has been tested only on the bench-scale level. There are no pilot plants or commercial plants.

The SNPA/Topsoe Process[22]--The Topsoe process uses the SO_2-laden stream from the Claus incinerator. This stream is first cooled in a wasteheat boiler, then passed over a vanadium oxide-base catalyst to oxidize SO_2 to SO_3 with a 95 percent yield. The gas is cooled further and concentrated. In an absorber, the SO_3 is converted to 80 weight percent H_2SO_4, which is evaporated by heat from incoming gases to 94 weight percent H_2SO_4. The H_2SO_4 is formed without the sulfuric acid "mist" usually formed in the wet-contact process for making H_2SO_4.

One Topsoe plant was built in Lacq, France, in 1965 for a 100 lt/day Claus plant. There are no other commercial installations. The Lacq plant is reportedly 90 percent efficient.

The Shell Flue Gas Desulfurization (SFGD) Process[36,37]

The Shell flue gas desulfurization process is especially suited for application to a refinery because of the availability of hydrogen. The process is also being considered by the utility industry.

In the Shell process, the cooled flue gas from a Claus incinerator is passed over a copper oxide-on-alumina catalyst to absorb SO_2 according to the following reaction:

$$SO_2 + \frac{1}{2} O_2 + CuO \rightarrow CuSO_4 \qquad (1)$$

About 90 percent of the SO_2 in the flue gas is absorbed.

Two reactors are alternately in the absorption or regeneration stage. A spent bed is regenerated with hydrogen which reduces copper sulfate to elemental copper:

$$CuSO_4 + 2\ H_2 \rightarrow Cu + SO_2 + 2\ H_2O \qquad (2)$$

The elemental copper is oxidized to copper oxide by oxygen in the incoming flue gas. Because of hydrogen's extreme flammability, the reactor is purged with inert gas before and after regeneration. The SO_2 produced during regeneration is routed to the front of the Claus unit.

The cost of an SFGD unit is about 250 percent that of the parent Claus unit. The most promising application of the process is in a larger refinery where it might be used for the cleanup of all stack gases from process heaters (if they can be collected and sent to one or two stacks) and fluid catalytic cracking regeneration, as well as from the Claus unit itself.

Particulates do not affect the operation of a SFGD unit, and for this broad application the process can be designed to remove SO_x and NO_x simultaneously. This further application of the SFGD will be discussed more thoroughly in Section 3.2.3.7.

The Westvaco Process[22,38]--The Westvaco process utilizes a fluidized bed of activated carbon to remove SO_2 from the stack gas of a Claus unit incinerator. The activated carbon catalyzes the conversion of sulfur dioxide, oxygen and water vapor in the incinerated gas to sulfuric acid. The treated gas contains less than 200 ppmv SO_2.

The bed is regenerated with hydrogen sulfide in a regenerator/stripper. The hydrogen sulfide is obtained from the feed stream to the Claus unit. The regenerator/stripper may be designed to produce elemental sulfur or a concentrated SO_2 stream for recycle to the Claus unit.

To regenerate SO_2, the hydrogen sulfide first converts a portion of the absorbed SO_2 to elemental sulfur. The sulfuric acid/sulfur mix is then heated to produce SO_2.

Production of an elemental sulfur product is similar to that in the Sulfreen process. An excess of H_2S reacts with the H_2S to form elemental sulfur which is then vaporized from the bed.

No reliable cost figures are available for the Westvaco process. The process has not yet been demonstrated commercially.

The Pritchard Ammonium Bisulfate/Ammonium Thiosulfate Process[33]--In this process, the sulfur compounds in the Claus tail gas are oxidized to SO_2 and absorbed by contact with a weak aqueous solution of ammonia. The resultant solution of ammonium bisulfite, ammonium sulfite, and ammonium sulfate salts is converted to ammonium thiosulfate in an ATS reactor.

Capital expenditure for a 20,000 t/yr factility is about 75 percent that of the parent Claus unit. Clean gas from the unit contains less than 900 ppmv SO_2. The first commercial installation of the process is expected to start up in December 1979.

The BSR/Selectox I Process[33]--Initial treatment of the Claus tail gas in the BSR/Selectox I process is the same as that in the BSRP: the tail gas is reacted with a hot reducing gas in a catalyst bed to convert all sulfur species to H_2S by hydrogenation or hydrolysis. In the BSR/Selectox I process, the H_2S-rich stream is then cooled in a contact condenser to minimize water partial pressure.

The cooled stream is then mixed with air and passed over the BSR/Selectox catalyst to selectively oxidize the H_2S to elemental sulfur, which is removed by condensation. The overhead gas stream is incinerated.

Sulfur recovery from this process is normally greater than 98 percent. A recovery rate greater than 99 percent can be achieved by passing the oxidized streams through an additional Claus stage before incineration.

Investment for a plant to treat the tail gas from a 100 lt/day sulfur plant is $1.7 to $2 million.

The first commercial BSR/Selectox I plant began operation in 1978 in Germany.

The Mineral and Chemical Resource Company (MCRC) Limestone Slurry Sulfur Recovery Process[33]--The MCRC Limestone Slurry process treats the tail gas from the Claus plant incinerator by contacting it with a limestone slurry. The gas is contacted in each of the three phases (solid, liquid and gas) in a high energy device. Each contacting stage typically reduces the sulfur dioxide level more than 90 percent for a final efficiency of 99.9 percent.

The solid product consists of about 85 percent calcium sulfite, 10 percent calcium sulfate (gypsum) and 5 percent unreacted limestone. It does not have to be ponded; in fact, studies have shown it to be non-hazardous and beneficial to crops when applied at a rate of 3-10 tons per acre.

A typical MCRC plant consists of the contactors, a mist eliminator, a ball mill for grinding limestone, a central pump, and a filter for dewatering the solids, plus miscellaneous pumps, storage bins, etc. One U.S. plant has operated successfully since 1976.

IFP Catalytic Incineration[33]--A catalyst can be used to reduce the amount of energy necessary for incineration of Claus tail gas. The RS-103 and RS-105 catalysts promote the selective oxidation of sulfur compounds to sulfur dioxide. Typical outlet values of H_2S are less than 5 ppmv, those for COS and CS_2 combined are less than 150 ppmv.

Catalyst life is 2 - 3 years. Energy savings are about 1 MM Btu/hr. This savings corresponds to more than ten times the cost of catalyst replacement.

Four IFP catalytic incinerators are operating on Claus plants. The first began operation in 1975.

3.2.2.3 Catalyst Regeneration

A method has been developed which controls SO_2 emissions from FCCU catalyst regenerators by stack gas scrubbing. The method can also be used to control SO_2 and particulates simultaneously. Exxon has four such scrubbers installed in its coastal refineries (Texas, Louisiana, and New Jersey).

These scrubbers operate by mixing the flue gas with a buffered aqueous scrubbing liquor. The liquor absorbs the SO_2; other processes separate the liquor from the gas stream. The clean gas is then routed to the stack. Most of the scrubbing liquid may or may not be regenerated and recycled, depending on the particular scrubbing process being used.

A nonregenerable process has been used for FCCU flue gas, and the spent scrubbing liquid handled by conventional wastewater treatment. It contains a high concentration of dissolved solids and salts and has a high chemical oxygen demand (COD). To date, scrubbers for controlling SO_x from FCC regneration have been used only where wastewater can be discharged into the ocean after treatment. A 50,000 bbl/d FCCU charging a feed with 2 weight percent sulfur would generate as much as 60 - 70 tons of sludge per day.[29]

Exxon's operations have shown that 95 percent of the SO_x and 90 percent of the particles can be removed by a scrubber.[39] They believe that the cost of controlling both particulates and SO_x by scrubbing is less costly, both in initial investment and maintenance, than a combination of desulfurization and ESP's. The space requirements are also less. Actual comparisons of costs, energy requirements, and secondary effluent disposal are not available.

3.2.2.4 Boilers and Process Heaters

SO_x Removal--Emissions of SO_x from boilers and process heaters can be minimized by routing the flue gas to an integrated sulfur removal facility. Two such units are the IFP-150 and the Aquaclaus (dicussed in the preceding sections).

NO_x Removal--NO_x emissions can be reduced by several tail gas cleaning methods. Removal of NO_x from tail gas is, however, inherently more difficult than controlling NO_x by the combustion modifications discussed in Section 4. The principal difficulties are the large amount of hot gas to be handled, the dilute concentration of NO_x, interferences by other pollutants and the high power consumption. Three methods for removal of NO_x from stack gases are gas scrubbing, catalytic reduction and thermal reduction with added ammonia. Because of economic considerations, only thermal reduction with added ammonia appears promising.[14]

Gas Scrubbing[14]--Wet and dry scrubbing techniques for removal of SO_x also remove most of the NO_2 and an equivalent amount of NO which react to form N_2O_3. Because significant amounts of NO_2 form only after the NO in the stack gas meets the oxygen in the atmosphere, the low proportion of NO_2 in the gas limits the effectiveness of these processes. The NO_x removal efficiency can be improved by oxidizing part of the NO to NO_2. Air oxidation is cheaper than the use of oxidizing agents such as permanganate or chlorine oxides.

Reactive salts of metals such as iron can form chelates with NO, but the chelating agents have high molecular weights and low solubility. Sodium sulfite can reduce both NO and NO_2 to molecular nitrogen in a special rotary atomizer. However, oxygen must be removed from the flue gas at great expense.

Catalytic Reduction[14]--Catalytic reduction may be more practical than scrubbing for removing small amounts of nitrogen. In the process, NO_x is combined with a reducing gas such as ammonia or hydrogen sulfide to form molecular nitrogen in the presence of a catalyst. Ammonia is less poisonous to most catalysts than is hydrogen sulfide. Hydrocarbons, hydrogen, or carbon monoxide can also be used as reducing agents if oxygen is removed.

A new Japanese process has two beds of a base metal catalyst on alumina and a slight excess of ammonia. The first bed, at 572°F, reduces the NO_x. The remaining 50 ppm ammonia is removed on the second bed. The catalyst is less sensitive than platinum to sulfur, but particulates must be removed.

Thermal Reduction with Added Ammonia[14]--Controlled addition of ammonia to an oxygen-containing flue gas under strictly controlled conditions at 1,300° to 1,900°F can selectively reduce 50 to 70 percent of the NO_x remaining after combustion controls. This "thermal denox" process is a balance between two gas-phase reactions: ammonia reduces NO to N_2 in the presence of the oxygen in the flue gas and ammonia is simultaneously oxidized to NO. When conditions are carefully controlled, a major portion of the NO_x can be reduced with little ammonia left over. This process is more expensive than combustion modifications but can supplement these modifications when stricter control of NO_x is required.

3.2.3 Control Technology from Other Industries

Some control methods which have been developed primarily for other industries can also be used in the petroleum refinery industry with some degree of adaptation. This is especially true of methods developed by the electric utility industry for flue gas desulfurization. Some can be applied to the flue gas from a Claus incinerator. Another with accompanying NO_x control can be adapted for the flue gases from process heaters; still others might be used to control sulfur emissions from FCC regenerators.

3.2.3.1 Sulfur Recovery

The Chiyoda Thoroughbred 101 Process[27]--The Chiyoda Thoroughbred 101 process was developed for desulfurization of flue gases. For application to a Claus unit, the tail gas is first incinerated, cooled, and scrubbed with water. About 97 percent of the SO_2 in the tail gas is then absorbed by dilute sulfuric acid in an absorber. The overhead stream is passed without further treatment to the atmosphere. If the Claus tail gas contains less than 15,000 ppmv SO_2, an emission rate of less than 500 ppmv SO_2 can be achieved. A level of 250 ppmv is required to meet Federal New Source Performance Standards.

The bottoms from the absorber pass to an oxidizer where they are mixed with air over an inexpensive nonpoisonous catalyst. The majority of the acid returns to the absorber; a bleed stream is routed to a crystallizer. Limestone is mixed into the acid in the crystallizer to form gypsum crystals which are collected, dried, and stored.

Because there is not a good market for gypsum in the United States, this method will probably not be a significant one for the refining industry.

The USBM Citrate Process[27]--Citrate flue gas desulfurization is a regenerable process in which an aqueous sodium citrate solution absorbs sulfur dioxide from flue gas. The method is being developed primarily for flue gases from utility boilers, but appears to be applicable to the flue gas from a Claus plant incinerator.

As the flue gas flows through the absorber, the SO_2 in the gas is dissolved in the citrate liquor. Once dissolved, it reacts with water to form sulfurous acid (H_2SO_3). The sulfurous acid ionizes to form hydrogen ion (H^+) and bisulfite (HSO_3^-). The citrate enhances these reactions by removing hydrogen ions from solution. Some of the sulfite is oxidized to sulfate. Desulfurized flue gas is reheated and vented to the atmosphere.

The absorber liquor is regenerated in a reactor by contacting it with hydrogen sulfide (H_2S) to form elemental sulfur. The H_2S can be obtained from the feed streams to the Claus unit. The sulfur slurry formed in the reactor then flows to a digester where it is mixed with a small by-pass stream of SO_2-rich citrate liquor from the absorber. This liquor consumes any unreacted hydrogen sulfide. Gases vented from the reactor and the digester contain small quantities of H_2S, CS_2, and COS. These gases are incinerated.

The sulfur slurry from the digester is separated from the citrate solution by flotation with air in a separate vessel. A flotation agent such as kerosene can be used to increase the sulfur solids concentration of the froth to 50 percent. Regenerated citrate solution is returned to the absorber.

To remove accumulated sulfates from the system, a small bleed stream is diverted from the regenerated citrate stream and treated for sulfate removal. Sodium sulfate decahydrate (Glauber's Salt) is continuously removed from solution and recovered for sale or disposal. Lean citrate solution is returned to the system.

Entrained air is released from the froth by agitation and then incinerated. The sulfur/liquor mixture is heated in a shell and tube heat exchanger to melt the sulfur. The molten sulfur is separated by gravity from the citrate solution.

An important environmental consideration is disposal of the Glauber's Salt. A long-term solution for disposal of this sulfate by-product has not been identified.

It has been estimated that a citrate plant for an 85 lt/day Claus plant would cost 250 percent of the cost of the parent Claus unit. No commercial citrate plants have yet been built; a commercial-scale demonstration plant for a utility was scheduled to begin operation in mid-1979.

One of the major drawbacks of the use of the citrate process by the utility industry is the expensive manufacture of H_2S. Because the required H_2S is readily available at a Claus plant, the process may be more suited for use by the refining industry.

The Townsend Process[22]--The Townsend process was proposed as a method for the desulfurization of high-pressure natural gas. It is quite similar to the IFP-1,500 process. The Claus reaction takes place in an organic solvent, such as triethylene glycol, at an elevated temperature. Liquid sulfur is drawn from the bottom of the vessel.

The process may be applied directly to the Claus tail gas. It does not, however, remove COS or CS_2 and, therefore, can not achieve a very low sulfur emission rate.

The Townsend process has been tested in pilot plants, but as of mid-1978 no commercial plants had been built.

The Lurgi-Claus-Abgas-Schwefelgewinnung (LUCAS) Process[40,41]--The LUCAS process will probably be used primarily to treat lean H_2S streams for which the Claus process is unsuitable. It also appears to be well-suited for Claus tail gas cleanup.

The tail gas is first incinerated, then cooled and treated with hot granulated coke to covert impurities to SO_2, Co_2, or N_2:

$$2\ SO_3 + C \rightarrow 2\ SO_2 + CO_2 \tag{1}$$

$$H_2S + 1\tfrac{1}{2}\ O_2 \rightarrow SO_2 + H_2O \tag{2}$$

$$2\ NO + C \rightarrow N_2 + CO_2 \tag{3}$$

$$O_2 + C \rightarrow CO_2 \tag{4}$$

The SO_2 is removed from the off-gases with an aqueous alkali phosphate solution which can be regenerated by heating:

$$Na_2HPO_4 + H_2O + SO_2 \rightleftharpoons NaH_2PO_4 + NaHSO_3 \tag{5}$$

Because oxygen and SO_2 have been removed from the tail gas, no sulfate is formed.

The off-gas from a LUCAS absorber reportedly contains less than 200 ppm SO_2, less than 150 ppm COS and CS_2, and practically no H_2S. Recycling the SO_2 to the Claus unit can increase the sulfur yield up to 99.9 percent.

Investment cost for a LUCAS unit is expected to be 75 - 80 percent that of the parent Claus Unit. It is estimated that 9.1 kwh's of electricity, 1,900 lb steam and 2,170 Btu fuel gas are required for the production of 200 lb sulfur from a 50 t/d Claus unit with a 75 percent H_2S feed. There is one semi-commerical LUCAS plant in West Germany.

The Takahak Process[33]--The Takahak process is quite similar to the Stretford and could be used in its place in many applications. It is now being used to treat fermented sewage, coke oven gas and chemical plant waste gas.

The tail gas from the Claus unit may be fed to an absorber tower which contains sodium carbonate and sodium 1,5-naphthoquinone, 2-sulfonate as a redox catalyst. Hydrogen sulfide in the tail gas reacts with the sodium carbonate to form sodium bisulfide and sodium bicarbonate. The bisulfide is oxidized by the catalyst to form finely divided sulfur which is filtered from a slip stream.

The naphthoquinone sulfonate which was reduced to naphtho-hydroquinone sulfonate is regenerated with bubbling air in a regenerator. The vent stream from the regenerator contains no H_2S and can be released to the atmosphere.

Up to 99.9 percent of the H_2S in a gas stream can be removed by this method. Capital costs for a Takahak plant are relatively low and the only utility needed is electricity for pumping. The catalyst is cheap and easily available.

3.2.3.2 Catalyst Regeneration

Several FGD methods used by the utility industry have been proposed for use on FCC regenerators.[29] They are described below. In addition, some of the regenerable processes discussed in Section 3.2.3.1 for treatment of the Claus unit tail gas may also be applicable. One of the processes described below simultaneously removes SO_x and particulates from the flue gas.

The Lime/Limestone Flue Gas Desulfurization Process[42]

Lime or limestone flue gas desulfurization processes are the most widely used FGD systems. The systems are very similar; they consume large quantities of feed material and produce large quantities of waste sludge, but have relatively low operating costs and are highly reliable. An SO_2 removal efficiency of greater than 90 percent has been demonstrated.

In the feed preparation area, pebble lime (CaO) is slaked with water to yield a dilute solution of calcium hydroxide ($Ca(OH)_2$). Limestone ($CaCO_3$) is ground in wet ball mills and is then slurried with water. Both slaked lime and limestone produce calcium ions.

Absorption takes place in a wet scrubber. The SO_2 is absorbed in water and reacts to form sulfite ions ($SO_3^=$). The desulfurized flue gas is released. The sulfite ions begin a series of reactions and eventually coprecipitate with calcium as a solid solution.

The precipitation reactions go to completion in an effluent hold tank. The liquid from the hold tank is recirculated to the absorber. The bleed stream is continuously drawn from the hold tank for dewatering, solids concentration, and disposal. A thickener is usually added to the bleed stream for primary dewatering; the stream may then be vacuum filtered or centrifuged. The sludge may be ponded on-site or trucked off-site to a landfill.

A major design option is the choice of lime or limestone. Limestone is less expensive than lime, but it is not used as efficiently by the process; therefore, there is more feed material consumption and more waste sludge production if limestone is used. Procedures which improve limestone utilization also increase capital and operating costs.

Lime systems are usually more expensive to operate, however, because of the high cost of lime. Lime systems may be preferred where space is limited for feed material processing and/or waste sludge disposal. Capital and utility costs are also lower for a lime system. The choice between lime and limestone is also influenced by the availability of raw materials.

Several vendor companies market processes for the stabilization of waste sludge. They all involve the addition of various substances to the sludge to make it structurally stable and leach-resistant. Stabilized sludge is easier to transport and makes a landfill which can later be used productively. An alternative to simple disposal is the oxidation of the bleed stream to gypsum. The purified gypsum can then be sold if a market can be found.

Costs of raw materials and utilities for lime/limestone systems are generally lower than for regenerable processes, although more raw materials are required. Annual operating costs of a lime system are about seven percent higher than those of a limestone system.

The Dual Alkali Flue Gas Desulfurization Process[43]--The dual alkali (or double alkali) flue gas desulfurization process can be used to overcome the scaling problem inherent in lime/limestone FGD systems while retaining the convenience of solid waste disposal. There are 53 operating dual alkali systems in the United States and Japan; several more are under construction.

These systems can achieve SO_2 removal efficiencies of greater than 90 percent. The capability for more than 99 percent removal of SO_2 has been demonstrated. The dual alkali process itself is capable of greater than 98 percent particle removal.

Absorption of SO_2 from the flue gas takes place in a tray tower, or a venturi scrubber if simultaneous particle removal is desired. The SO_2 in the flue gas reacts primarily with sodium sulfite (Na_2SO_3) to form sodium bisulfite ($NaHSO_3$). Some sulfite and bisulfite oxidize to sulfate. The desulfurized flue gas is reheated if necessary and released to a stack. A bleed stream of the scrubbing liquor is withdrawn continuously from the absorber and regenerated.

The sodium alkali in the bleed stream is regenerated in chemical mix tanks. Lime ($Ca(OH)_2$) or limestone ($CaCO_3$) is added to the liquor and the resulting calcium sulfite and calcium sulfate are precipitated and removed as a slurry.

The slurry from the regeneration step is very dilute. It is dewatered first in a clarifier thickener and then on a vacuum filter. The solids cake on the vacuum filter is washed with several water sprays to remove up to 90 percent of the sodium salts from the cake. The cake is then ponded or used as landfill. Make-up sodium carbonate is added to the clarifier thickener liquor which is routed to the absorber.

Slaked lime ($Ca(OH)_2$) is generally used to regenerate the scrubber effluent. Limestone ($CaCO_3$) has been used as the regenerant, but impurities and the lower calcium utilization rate are major problems.

Loss of soluble sodium and nonsulfur calcium salts can create water pollution problems and also a loss of raw materials. Therefore, water can be added to the system only to replace that lost through evaporation or in the solid waste product. Also, retention of soluble salts by the solid waste must be minimized.

Sludge from the dual alkali process must be fixed chemically to decrease its permeability and leachability, or it must be disposed of in well-designed lined ponds. The thixotropic nature of the calcium sulfite may make land reclamation difficult.

Dual alkali systems are economically competitive with lime/limestone systems. The equipment required for a dual alkali system is similar to and perhaps less than that required for a lime/limestone system. Because of the higher moisture content of dual alkali sludge, a larger disposal area will be required than for a lime/limestone system.

3.2.3.3 Boilers and Process Heaters

In addition to the process described below, the processes proposed for control of SO_2 emissions from FCCU regenerators may also be applicable to the flue gases from boilers and process heaters.

The Shell Flue Gas Treatment (SFGT) process can be used to remove SO_x and NO_x simultaneously from all stack gas from process heaters (if it can be collected and sent to one or two stacks) and fluid catalytic cracking regeneration, as well as from a Claus unit.[44,45]

The SFGT process has demonstrated SO_2 and NO_x removal efficiencies of greater than 90 percent. The efficiency of the system is not affected by variations in the SO_2 or NO_x concentration.

Flue gas is drawn into the process upstream of any particle removal equipment. It is then mixed with ammonia and fed to a reactor which contains regenerated elemental copper on a series of parallel plates. The flue gas flows over the plates, not through them.

Upon initial exposure to the oxygen in the flue gas, the elemental copper is converted to copper oxide. Since copper catalyzes the oxidation of ammonia to NO_x, NO_x is actually produced in the reactor for the short time before all the copper has been converted. To minimize these NO_x emissions, the bed can be preoxidized with air or incompletely regenerated before it is returned to service, or injection of ammonia can be delayed.

The copper oxide then reacts with SO_2 to form copper sulfate. Maximum SO_2 removal occurs when the bed is fully converted to copper oxide. The removal efficiency steadily decreases to a breakthrough point when all the copper oxide has been converted to copper sulfate.

The reduction of NO_x to nitrogen begins as copper oxide is formed and increases rapidly as copper sulfate is formed because copper sulfate is the more effective catalyst. Maximum NO_x removal occurs at the point of SO_2 breakthrough.

The spent bed is regenerated by a reducing gas made up primarily of hydrogen. The hydrogen reduces copper sulfate to elemental copper and sulfur dioxide. Any copper oxide present is also reduced to elemental copper. Because of hydrogen's extreme flammability, the reactor is purged with an inert gas such as low pressure steam before and after regeneration. The SO_2 may be sold, processed into elemental sulfur or sulfuric acid, or routed to the front of the Claus unit. The primary waste from the process is water generated during the recycle step. This water contains 30 to 50 ppm dissolved SO_2.

The process requires approximately two moles of hydrogen per mole of SO_2 removed and one mole of ammonia per mole of NO_x removed. A heat credit may be realized by the process. Actual costs for an integrated SFGT system are not available because such a system has not yet been built at a U.S. installation. Due to the complexity of the process, space requirements are expected to be high. Retrofit application of the SFGT process might be difficult because of the duct work required.

3.3 References

1. Gary, J. H., and G. E. Handwerk. Petroleum Refining, Technology & Economics. Marcel Dekker, New York, New York, 1975.

2. Elkin, H. F., and R. A. Constable. Source/Control of Air Emissions, Hydrocarbon Proc., 51(10):113, 1972.

3. Dickerman, J.C., et al. Industrial Process Profiles for Environmental Use, Chapter 3. Petroleum Refinery Industry. EPA 600/2-77-023C, Radian Corporation, Austin, Texas, January, 1977.

4. Bryant, H. S. Environmental Needs Guide to Refinery Sulfur Recovery. Oil Gas J., 71(13):70-76, 1973.

5. U. S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. 3rd Edition with Supplements 1-8. AP-42, PB 275, Research Triangle Park, North Carolina, 1977.

6. Groenendaal, W., and H.C.A. Van Neurs. Shell Launches Its Claus Off-Gas Desulfurization Process. Petrol. Petrochem. Int., 12(9):54, 1972.

7. Radian Corporation. A Program to Investigate Various Factors in Refining Siting. Federal Energy Administration, Washington, D. C., 1974.

8. Sussman, V. H. Atmospheric Emissions from Catalytic Cracking Unit Regenerator Stacks. Report No. 4. Joint District, Federal and State Project for the Evaluation of Refinery Emissions and Western Oil and Gas Association, Los Angeles, California, 1957.

9. Little, Arthur D., Inc. Screening Study to Determine Need for SO_x and Hydrocarbon NSPS for FCC Regenerators. EPA-458/3-77-046, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, August, 1976.

10. Radian Corporation. Control Techniques for Volatile Organic Emissions from Stationary Sources. EPA-450/2-78-022, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

11. Nelson, W. L. Petroleum Refinery Engineering. 4th Edition. McGraw-Hill, New York, New York, 1958.

12. American Petroleum Institute, Committee on Refinery Environmental Control. Hydrocarbon Emissions from Refinery. API Pub. No. 928, Washington, D. C., 1973.

13. Laster, L. L. Atmospheric Emissions from the Petroleum Refining Industry. EPA-650/2-73-017, PB 225 040, Control Systems Lab, Research Triangle Park, North Carolina, 1973.

14. American Petroleum Institute, Division of Refining. Manual on Disposal of Refinery Wastes, Volume on Atmospheric Emissions. API Pub. No. 931, Washington, D.C., 1976.

24. Grancher, P. Advances in Claus Technology, 2 Parts. Hydrocarbon Proc., 57(7):155, 1978, Part 1; Hydrocarbon Proc., 57(9):257, 1978, Part 2.

25. Beavon, D. K. Add-On Process Slashes Claus Tailgas Pollution. Chem. Eng., 78(28):71-73, 1971.

26. Catalytic, Inc. The Stretford Process. Philadelphia, Pennsylvania, 1976.

27. Processes Clean Up Tail Gas. Oil Gas J., 76(35):160-166, 1978.

28. Bailey, E. E. Power Plant Flue Gas Desulfurization by the Wellman-Lord SO_2 Process. Part II - Continuing Progress for Wellman-Lord SO_2 Process. In: Flue Gas Desulfurization Symposium, Atlanta, Georgia, November 1974. EPA-650/2-74-126a, b. U. S. Environmental Protection Agency, Office of Reserach and Development, Research Triangle Park, North Carolina, December 1974, pp. 745-759.

29. Vasolos, I. A., et al. New Cracking Process Controls FCCU SO_x. Oil Gas J., 75(26):141-148, 1977.

30. Rheaume, L., et al. New FCC Catalysts Cut Energy and Increase Activity. Oil Gas J., 74(20):103-107, 110, 1976.

31. Fogiel, M., Ed. Modern Pollution Control Technology, Vol. 1: Air Pollution Control. Research & Educators Education Associates, New York, New York, 1978.

32. Atmospheric Emissions from Petroleum Refineries. A Guide for Measurement and Control. PHS No. 763, Public Health Service, Washington, D. C., 1960.

33. Conser, R. E. Here's a New Way to Clean Process Gases. Oil Gas J., 72(13):67-68, 70, 1974.

34. Barthel, U., et al. Sulfur Recovery in Oil Refineries Using IFP Processes. Adv. Chem. Serv., 139:100-110, 1975.

35. Parthasarathy, R. and L. P. Van Brocklin. Applications of the Phosphate Process to Heavy Oil Refining. Paper No. AM-78-48. Presented at the 1978 NPRA Annual Meeting, San Antonio, Texas, 1978.

36. Conser, R. E. and R. F. Anderson. New Tool Combats SO_2 Emissions. Oil Gas J., 71(44):81-86, 1973.

37. Dry Process for SO_2 Removal Due Test. Oil Gas J., 70(34): 67-70, 1972.

38. Ball, F. G., et al. Claus Process/Gaseous Wastes. Hydrocarbon Proc., 51(10):125-127, 1972.

39. Controlling SO_x Emissions from Fluid Catalytic Cracking (FCC) Units. Wet Scrubber Newsletter, (48):6, 1978.

40. Coke Key to Cleaning Claus Unit Tail Gas. Oil Gas J., 74(47):142-144, 1976.

41. Doerges, A., K. Bratzler, and J. Schlauer. LUCAS Process Cleans Lean H_2S Streams. Hydrocarbon Proc., 55(10):110-111, 1976.

42. Hulman, P. B. and J. M. Burke. The Lime/Limestone Flue Gas Desulfurization Processes, Draft Final Report. EPA Contract No. 68-02-26-08. Radian Corporation, Austin, Texas; U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

43. Gibson, E. D., T. G. Sipes, and J. C. Lacy. The Dual Alkali Flue Gas Desulfurization Process, Draft Final Report. EPA Contract No. 68-02-26-08. Radian Corporation, Austin, Texas; U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978.

44. Arneson, A. D., F. M. Nooy, and J. B. Pohlenz. The Shell FGD Process Pilot Plant Experiences at Tampa Electric. In: Flue Gas Desulfurization Symposium, Fourth, Hollywood, Florida, November 1977, EPA-600/7-78-058a, b. Franklin A. Ayer, comp. Research Triangle Institute, Research Triangle Park, North Carolina, March 1978. pp. 752-793.

45. Stern, R. D., et al. Interagency Flue Gas Desulfurization Evaluation, Draft Final Report. EPA Contract No. 68-02-26-08, Task 16. Radian Corporation, Austin, Texas; U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1977.

4.0 EMISSION REDUCTION THROUGH PROCESS MODIFICATION

4.1 Alternative Operating Practices and Conditions

Refinery operations are routinely modified to meet product specification requirements, product marketing trends, feedstock availablity constraints, and operating cost goals. The operating choices made include both deliberate actions concerning processing alternatives (such as which catalyst to use or what cutpoint to pick) and more subtle actions, mainly in the energy conservation areas (such as attention to steam leaks or furnace efficiency). These choices can also affect the overall refinery emissions.

This subsection summarizes the effects on emissions of some of these alternative operating practices.

4.1.1 Catalytic Cracking Catalysts Regeneration[1,2,3,4,5]

In older FCCU regenerators, the highly exothermic oxidation of CO to CO_2 is avoided because the resulting high temperatures can damage regenerator equipment, permanently deactivate the catalyst, and damage downstream equipment as well. To avoid this oxidation, flue gas from the regenerator generally contains little oxygen and large, nearly equal, amounts of CO and CO_2.

For several years, emphasis has been placed on promoting the oxidation of CO to CO_2 in the regenerator while controlling peak temperatures. This oxidation can be promoted by simply raising the temperature of the regenerator and increasing the oxygen partial pressure. A cooling system consisting of steam and water sprays helps prevent equipment damage if combustion control is lost.

Older FCC regenerators were designed for operation at temperatures up to 1150°F; the introduction of newer, more coke-sensitive catalysts necessitated higher temperatures. By 1976, 30 percent of all FCC regenerators were operating at 1300°F. High-temperature conversion of CO to CO_2 generally occurs at 1400-1500°F.

With high temperature regeneration, coke is burned from the catalyst more efficiently, therefore yield from the FCC unit is increased. The carbon monoxide level in the exit gas from the regenerator can be reduced to well below 500 ppm; therefore a CO boiler is no longer necessary for CO emission control.

Complete combustion of carbon monoxide within the regenerator offers other emissions benefits in addition to reducing carbon monoxide to less than 500 ppm: elimination of the need for a carbon monoxide boiler reduces other emissions since auxiliary fuel burning is not required and NO_x- producing carbon monoxide boiler temperatures are avoided. Recovery of additional heat in the regenerator reduces (and in some cases eliminates) the need for a FCC preheater and its associated emissions.[6]

Several new catalysts, or promoters, have been introduced in the last several years to promote the combustion of CO to CO_2. A promoter may be chosen to promote complete combustion or partial combustion where metallurgy cannot withstand the higher temperatures. Partial combustion can also be used in situations where the CO is needed as fuel.

There are three types of promoters now in use. First to be offered were catalysts modified with a small concentration of noble-metal promoting agent. The metal content is so small that recovery from discarded catalyst is uneconomical. The degree of promotion can be varied. The second type of promoter is a liquid additive which is injected into the FCC regenerator combustion zone. The third type is a solid promoter which can be mixed with make-up catalyst in varying proportions.

In situations where partial combustion is needed, it is possible to combine high temperature regeneration with the CO boilers. For this combined operation, the degree of high-temperature regeneration, and the final temperature, can be controlled by the amount of promoter used. The partial loss of CO to the CO boiler can be somewhat compensated by the high temperature of the gas that does enter the boiler. Supplemental fuel to the boiler is still required, but its cost is offset by the increased product yield in the FCC unit.

In 1975, the cost of converting a relatively modern FCCU with stainless steel cyclones to high-temperature regeneration was $50,000 to $300,000. Cost of a CO boiler for the unit was perhaps $2 million to $3 million.

Other FCC operations which affect regenerator emissions are the amount of recycle and the stripping steam rate. Higher recycle rates produce more flue gas, but the net effect is negligible when compared to the impact of recycle on yields and operating costs. Similarly, insufficient stripping steam allows hydrocarbons to enter the regenerator to produce more flue gas and possible unstable operation. In this case, the impact of stripping steam rate on the entire unit's performance provides incentives for the reduction of emissions.

Operators of thermofor catalytic crackers (TCC) can achieve the lowest emissions by preventing upsets, which can cause releases of hydrocarbons and other gases through the various vent stacks. Stable operation is important to refiners for efficiency and product specification reasons, so there is no conflict with environmental goals.

One aspect of TCC operations which does conflict with environmental aims is the proper operation of elutriator systems. Elutriators remove catalyst fines from a slip stream of catalyst. Maintaining the elutriator in proper condition does not improve TCC performance. Fines which are not removed by the elutriator are vented to the atmosphere through the surge separator stack.

4.1.2 SO_x Removal in the FCC Regenerators[7,8]

Amoco has developed a catalyst which reduces the amount of sulfur leaving the regenerator as SO_2. The catalyst holds the sulfur until it is returned to the reactor, where it is released and converted to H_2S. The H_2S leaves the reactor with the cracked product and is later converted to sulfur in the Claus plant; the regenerated catalyst returns to the regenerator.

Cost for the 60 to 75 percent reduction in SO_x emissions with this method in a new facility is estimated at 3¢/bbl, compared to 22-24¢/bbl for stack-gas scrubbing and up to 27¢/bbl for feed hydrosulfurization. The use of the catalyst for SO_x control is also less expensive than other methods of retrofit applications.

4.1.3 Combustion Modification for Control of NO_x[9,10,11]

Of the oxides of nitrogen, only NO and NO_2 are of environmental concern. In combustion sources, NO may be produced either by the fixation of atmospheric nitrogen in the flame (thermal NO_x) or by the oxidation of a portion of the nitrogen in the fuel (fuel NO_x). NO_2 from combustion sources is produced as the NO combines with oxygen in the atmosphere. Refining sources of thermal NO_x and fuel NO_x are given in Table E4-1.

TABLE E4-1. REFINING SOURCES OF THERMAL NO_x AND FUEL NO_x

Classification	Source	Thermal NO_x	Fuel NO_x
High Temperature	Power boilers firing - gas	Present	Possible
	Power boilers firing - oil	Present	Possible
	Power boilers firing - coal	Present	Strong
Internal Combustion	Engines	Present	Unlikely
	Turbines	Strong	Possible
Moderate Temperature	CO boilers	Present	Present
	Coke and residual fuels	Present	Present
	Catalyst regeneration	Unlikely	Present
	Incineration	Present	Present
Process Heating	Gas cracking	Present	Possible
	Oil cracking	Unlikely	Possible
	Oil heating	Unlikely	Possible

Source: Reference 9.

Fuel NO_x forms more readily than does thermal NO_x because of the relative weakness of the carbon-nitrogen bond as compared to the extreme stability of the nitrogen-nitrogen triple bond. About 80 percent of the nitrogen in fuels containing less than 0.1 percent nitrogen goes to NO_x. For fuels containing more than 1.5 percent nitrogen, about 20 percent of the fuel nitrogen is converted to NO_x. The mechanism of formation of fuel NO_x is essentially the same for all types of bound N.

Control of fuel NO_x is not a major concern in refineries for several reasons. First, refinery fuels are typically low in nitrogen content since coal is rarely used. Second, since the percent conversion of fuel nitrogen to NO_x increases as the nitrogen content decreases, the use of low-nitrogen fuels is not by itself an effective method for reducing NO_x emissions. Fuel NO_x emissions are also relatively unaffected by combustion modifications. Therefore, combustion modifications for the control of NO_x emissions from refineries are mainly concerned with the reduction of thermal NO_x. Fuel NO_x may become more significant, however, as thermal NO_x values are minimized in boilers and as air quality regulations become stricter.

4.1.3.1 Boilers, Furnaces, and Process Heaters

Combustion modifications for NO_x control on boilers, furnaces, and process heaters are of three general types: lowering the flame temperature, limiting the amount of excess air, and limiting the residence time within the flame. Control of NO_x is often counter to a high thermal efficiency and contributes to the emission of other undesirable substances; therefore, compromises must often be made.

Flame temperature is always greater than furnace temperature because of the immediate dissipation of heat. Flame temperature is determined by combustion chemistry and is dependent on the type of fuel used. If all other factors are equal, flame temperature is lowest for gas, higher for oil and highest for coal. Flame temperature also depends on the amount of aeration of the fuel: a well aerated blue flame has a higher temperature and thus produces more NO_x than does a less-well-aerated yellow flame. Theoretically, a reduction of only 70°F in the flame temperature can cut NO_x emissions by one-half.

Excess air contributes to NO_x emissions because of the availability of oxygen for NO_x-forming reactions. It also contributes to a hotter flame. However, a lack of sufficient excess air will lead to the emission of unburned fuel, smoke, and carbon monoxide. A reducing zone in the fire box resulting from inadequate combustion air can lead to premature failure of tubes and fittings. On the other hand, a large excess of air can dilute the flame, decrease flame temperature, and thus decrease NO_x production.

Residence time (the time the gas is actually in the flame) is determined by the gas flow rate and the length of the flame. The flame length is directly proportional to heat release. Therefore, smaller burners with less heat release per burner reduce the residence time.

A number of specific combustion modifications for NO_x control have been devised. Those for refinery boilers are summarized in Table E4-2. Combinations of these methods have been shown to yield a smaller effect than the sums of the effects from the individual technologies. The effectiveness of some of the individual methods and some combinations at different boiler loads are shown in Table E4-3.

Low excess air firing is the simplest combustion modification for NO_x control. It does require more complex ductwork and instrumentation for monitoring emissions so that the proper level of excess air can be maintained. Emissions of unburned fuel, smoke, and carbon monoxide can be a problem. The application of low excess air firing to refinery furnaces is complicated by the extensive use of natural draft and dampers to control the air supply. If oil burners are to be fired with low excess air, the oil must be vaporized before ignition and combustion essentially carried out in the vapor phase. Heat for vaporizing the fuel oil can come from recirculating combustion products.

Flue gas recirculation can be a control method in its own right, as it reduces the temperature and dilutes the oxygen with no loss in thermal efficiency. The flue gas is injected directly into the flame zone. In small furnace tests, recirculation of 10 weight percent of the flue gas reduced NO_x emissions by 60 percent. Recirculation of 20 weight percent resulted in a 75 percent reduction in NO_x emissions.

TABLE E4-2. BOILER COMBUSTION MODIFICATIONS FOR REDUCTION OF NO_x EMISSIONS

Method		Gas Fired Units	Oil Fired Units
Low Excess Air	Rating	Good	Good
	Advantages	Improved efficiency; less power required	Improved efficiency; less power required; less chance of cold end deposits
	Disadvantages	More complex ducts and controls	More complex ducts and controls
Flue Gas Recirculation	Rating	Excellent	Good
	Advantages	Very effective; does not upset combustion	In moderation does not upset combustion
	Disadvantages	High initial cost; high operating cost; additional controls	High initial cost; high operating cost; additional controls; works mainly on thermal NO_x
Staged Combustion	Rating	Excellent	Very good
Two-stage combustion with over-fire air ports	Advantages	Inexpensive; very effective	Inexpensive; moderately effective
	Disadvantages	Longer flames; slight increase in excess air	Longer flames; slight increase in excess air

Continued

TABLE E4-2. Continued

Method		Gas Fired Units	Oil Fired Units
Staged combustion (Cont'd) Off-stoichiometric or biased firing	Rating	Very good	Good
	Advantages	No power; effective	No power; moderately effective
	Disadvantages	Slightly longer flames; small increase in excess air	Slightly longer flames; small increase in excess air
Direct cooling Lower preheat or water injection	Rating	Fair	Fair
	Advantages	Simple; no power	Simple; no power
	Disadvantages	Reduced unit efficiency; require equipment	Reduced unit efficiency; require equipment
Reduced load or oversized fire box	Rating	Very good	Very good
	Advantages	Simple; no power	Simple; no power
	Disadvantages	High initial cost	High initial cost; more radiant superheater
Burner modifications	Rating	Good	Very good
	Advantages	Simple; no power	Simple; no power
	Disadvantages	None	None

Source: Reference 9.

TABLE E4-3. REDUCTIONS OF NO_x EMISSIONS WITH COMBUSTION MODIFICATIONS AT VARIOUS BOILER LOADS

Combustion Modification		PERCENT REDUCTION IN NO_x EMISSIONS WITH														
		Low Excess Air			Staging			Low Excess Air and Staging			Flue Gas Recirculation			Possible* Combined Modifications		
(Percent Full Load)		85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60	85/105	60/85	50/60
Fuel Fired	Burner Arrangement															
Gas	Front Wall	13	24	7	37	30	30	48	42	36	-	-	-	43	42	36
	Horizontally Opposed	17	15	32	54	35	59	61	48	68	-	-	20	73	52	72
	Tangential	-	-	-	-	-	-	-	-	-	-	60	-	66	65	-
	Average	16	19	26	45	31	52	54	44	52	-	60	20	64	51	60
Oil	Front wall	27	20	28	29	20	20	39	32	21	46	31	-	50	41	21
	Horizontally Opposed	10	16	12	34	34	47	35	44	42	-	-	-	38	35	55
	Tangential	28	22	-	-	17	-	-	45	-	10	13	-	-	59	-
	Average	19	19	18	30	22	34	38	37	37	28	23	-	47	42	38

*Possible combination of modifications on the boilers tested.

Source: Reference 9.

Two-stage combustion reduces both the temperature and the availability of oxygen. The fuel is burned once with only 85 to 95 percent of stoichiometric air. The partially combusted gases are cooled and then burned again at a low temperature with 10 to 15 percent excess air injected through unused upper burners or through a "NO_x-port" located higher in the furnace. All variations of two-stage combustion involve firing some burners fuel-rich and others fuel-lean.

Flame temperature can be reduced by injection of steam, water, or a water-oil emulsion into the combustion zone. The oxygen concentration is also diluted when steam or water is used. Reducing air preheat also reduces the flame temperature. These methods do lower the thermal efficiency of the unit somewhat; the dilution effect can be enhanced with less loss of efficiency if a large amount of waste steam is injected instead of the same weight of water.

Reducing the load or the firing rate reduces NO_x emissions as does oversizing the combustion zone. The capital costs for this unused capacity are high.

In larger furnaces and boilers, fuel dispersion, primary/secondary air ratios, burner tilt, burner configuration, and burner spacing are important variables. Changes in burner arrangement will probably be small in furnaces with only a single line of burners.

Low excess air firing and off-stoichiometric firing are the easiest modifications to apply to an existing unit. Addition of NO_x-ports or the addition of flue gas recycle is frequently a major effort. Retrofit attempts are hampered by the large number of units and their diversity. The design of a particular unit or the lack of space for ductwork may be a severe restriction. Individual units must be tuned to avoid the problems of corrosion, reductive decarburization, and deposits on boiler tubes, flame instability, blowoff, flashback, combustion-driven oscillations and combustion noise or roar.

4.1.3.2 Internal Combustion Engines

There are several modifications for controlling NO_x emissions from internal combustion engines. The percent NO_x reduction and the limitations for each of these modifications are given in Table E4-4.

Modification of combustion chamber design now in use in diesels and in Honda gasoline-powered automobiles may include the use of a prechamber, turbulence chambers, or "energy cells." A prechamber provides a type of two-stage combustion with a very rich first stage and a very lean second stage. This arrangement is known as a "stratified charge" engine design. "Energy cells" provide controlled combustion to prevent high-peak pressures and rough operation. Internal exhaust recirculation, controlling oxygen availability, special low-NO_x combustors, and premixed, prevaporized and well-stirred external combustors are being studied for use on turbines.

In the diesel engine, an increase in the specific gravity of the fuel is accompanied by an increase in NO_x emissions. NO_x emissions from distillate oil-fired gas turbines are about twice as high as those from natural gas-fired turbines. In gas turbines, the effect of fuel composition on NO_x emissions may vary with fuel rate and the geometry of the combustion zone, so each design must be examined separately. Also, limited data suggest that fuel nitrogen is converted to NO_x at a high rate in gas turbines.

TABLE E4-4. ENGINE MODIFICATIONS WHICH REDUCE NO_x EMISSIONS FROM INTERNAL COMBUSTION ENGINES

	DIESELS		SPARK IGNITION		GAS TURBINES	
ENGINE MODIFICATION	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS	NO_x REDUCTION (Percent)	PENALTIES & LIMITATIONS
Combustion chamber design	40	Increased first cost	-	Not applicable	Under development	
Fuel properties	Variable	Availability of low nitrogen fuels; higher operating cost	Variable	Availability of low nitrogen fuels; higher operating costs	Variable	Availability of low nitrogen fuels; higher operating costs
Air/fuel ratio	-	Not applicable	30	Backfiring; reduced power	50	Increased fuel; decreased power
Exhaust recycle	50	Increased fuel; decreased power	50	Increased fuel; decreased power	Under development	
Fuel injection timing	40	Increased fuel; decreased power	-	Not applicable	-	Not applicable
Steam or water injection	50	Corrosion problems	50	Corrosion problems	75	Need deionized water; costly
Variable compression ratio	Under development		-	Not applicable	-	Not applicable

Source: Reference 9.

NO_x emissions can be controlled in gas engines by adjustment of the air/fuel ratio because gas engines operate with premixed homogeneous mixtures. The flame temperature is reduced with increasing air-fuel ratios, but too lean a mixture causes backfiring and loss of power and fuel efficiency. Diesel engines are not amenable to this modification because they do not have homogeneous mixtures and combustion occurs in fuel-rich zones. In turbines, the increased air/fuel ratio reduces NO_x emissions but it also decreases the turbine inlet temperature, causing a severe loss of power and increased fuel consumption.

Exhaust recycle can effectively control NO_x emissions from gasoline engines. However, the modification causes a decrease in the maximum power and efficiency of the engine. Additional piping and a control mechanism are needed at a modest extra cost. Current studies of combustor designs for gas turbines provide for internal exhaust recycle.

The pressure and temperature in an injected diesel engine can be varied by changing the timing of fuel injection. The point in the cycle at which fuel injection is started or the rate of fuel addition (or both) can be changed. Two-stage fuel injection is also possible. The effects of these variables on NO_x emissions from stationary engines have not been fully clarified; the changes will probably also affect power output and thermal efficiency of specific units.

Injecting water or steam with the air into the combustor of an engine reduces NO_x emissions, probably because of a reduction in the temperature of the flame surrounding the burning drops of atomized fuel. The modification works for diesel, gas turbine, and spark ignition engines. The amount of reduction depends on the water- or steam-to-air ratio and the method of injection. Deionized water must be used to avoid undesirable deposits, but it is not always available. Steam may be available as a by-product from other processes.

The compression ratio in a diesel engine can be changed by hydraulically raising or lowering the height of the top of the piston to maintain a preset peak combustion pressure in the chamber. Control of this pressure avoids the excessively severe cycles which occur frequently in conventional diesels and which may account for a disproportionate part of the NO_x emissions. Variable-compression pistons are more costly than conventional pistons and may require more maintenance.

4.1.4 General Refinery Operations

4.1.4.1 Efficient Gasoline Production

To produce the required volumes of gasoline at the octane levels specified, the refiner must find the optimum balance among such parameters as:

- reformer severity
- lead level
- MMT (if used) level in unleaded gasoline
- crude unit cut points (straight run versus naphtha, naphtha versus kerosene, and diesel versus gas oil)
- FCC conversion and severity

All of these factors influence emissions, but with the exception of lead and MMT, the effect on emissions of choosing one mix of parametric values over another is minimal when compared to the overall refinery balance. The maximum allowable levels of lead and MMT are regulated by the government. Nearly all refiners will operate at the maximum allowable levels of lead and manganese. Levels of these octane improvers less than the current maximums result in decreased gasoline volumes and increased fuel gas or fuel oil burning.

4.1.4.2 Alternate Processing of Intermediate Streams

In most refineries there is some excess capacity in several of the processing units. This excess is required to compensate for swings in crude composition or results from a desire to have additional processing flexibility.

In some refineries, portions of the olefin streams from cracking operations may be polymerized or alkylated. In the alkylation process isobutane is consumed. The choice between alkylation and polymerization is based on the values of isobutane, alkylate and polymer gasoline and the availability of isobutane. The choice between alkylation and polymerization has no significant effect on emissions.

Occasionally, portions of the diesel stream are charged to the catalytic cracker in an attempt to take advantage of idle cracking capacity and to make more gasoline. While opinions differ as to how beneficial this option is, it is certain to increase emissions to some extent. Lower boiling feedstocks do not crack as well as higher boiling stocks, but still must be heated and vaporized in the riser. Since diesel produces a negligible coke on catalyst, this heat is not recovered by combustion of coke in the regenerator and must be compensated by additional FCC preheater duty. Once again, higher emissions are accompanied by higher operating costs.

Some refineries have excess catalytic cracking and hydrocracking capacity. Processing flexibility is obtained by splitting the gas oil stream between these two units. While hydrocrackers do not have a flue gas stack, they do have somewhat higher fuel consumptions than FCC units (100,000 to 200,000 Btu per barrel of fresh feed versus 0 to 100,000 Btu per barrel of fresh feed.)[12] Hydrocrackers also consume 1200-2300 SCF of hydrogen per barrel of fresh feed.[13] Hydrogen manufacture produces emissions. The net effect on emissions of switching volumes of gas oil from one of these units to the other is not significant.

In some refineries, hydrotreating may be used as a substitute for solvent or chemical treating of products. In these instances the environmental problems associated with disposal of byproduct streams (such as acid sludge) are avoided.[13]

As a general rule, the refiner's actions to achieve stable operations which satisfy product volumes and qualities at minimum cost do not conflict with, and in most cases reinforce, efforts to reduce emissions.

4.1.4.3 Maximizing Overall Efficiency

Steam Generation and Usage--Boiler stack emissions may be reduced by maximizing efficiency of the overall boiler system design and operation, which is reflected in reduced fuel use. Use of high pressure steam is potentially more efficient than use of low pressure steam. The problem lies in proper design. One approach is to reduce steam pressure to the level required by fractionator reboilers, etc., by passing the high pressure steam through power generating turbines, and/or through turbines driving pumps and compressors.

A simple and energy-saving maintenance procedure is to ensure that all steam traps operate correctly, specifically that they pass condensate with minimum steam.

Insulation--Fuel usage in boilers and heaters can be reduced by proper heat insulation and weather protection of process equipment and piping which operate significantly above ambient temperatures. (Some equipment is insulated in colder climates simply to avoid winter freeze.) With increasing fuel prices, an "economic thickness" calculation will undoubtedly justify more insulation than in the recent past.

Fractionator Design and Control--The process engineer is familiar with the theoretical limits of fractionator operation:

(1) Minimum number of trays - total reflux (no products)

(2) Infinite number of trays - minimum reflux ratio (minimum tower diameter)

When fuel was cheaper, designs often approached "minimum trays" because of the relatively low cost of heating and cooling, and the high cost of equipment. Today, energy costs drive designs toward limit (2), a great number of trays, with reflux ratios (reflux rate:distillate rate) approaching the minimum value. Further economy can be realized in selected fractionation systems by "thermal coupling,"[14] computerized composition control,[15] and generalized system approaches.[16] One author states that a 10 percent decrease in distillation energy consumption in the USA would conserve 0.2 Quads (1.0 Quad = 10^{15} Btu) per year based upon 1976 figures. The saving is equivalent to 100,000 bbl of oil per day.[17]

In general, efficient energy utilization in the refinery is in accord with environmental goals.

4.2 Alternative Fuels[18]

Refiners traditionally have had a choice of natural gas, refinery gas, or distillate or residual fuel oils as fuel for refinery boilers and process heaters. The present trend is toward the heavier oils, both for economic reasons and because lighter oils are being reserved for smaller consumers with fewer emissions controls. This trend, however, results in higher emissions from refinery boilers and heaters.

Emissions factors for the use of natural gas and fuel oils in industrial boilers are found in Tables E4-5 and E4-6. According to these factors, particulate emissions from natural gas and No. 2 oil are independent of sulfur content, but increase with sulfur content for No. 4 oil and heavier oil (see footnote C of Table E4-6).

Sulfur dioxide emissions are, of course, directly related to sulfur content of the fuel gas or oil. Nitrogen oxide emissions result from oxidation of atmospheric and fuel bound nitrogen; the former increasing with combustion temperature, and the latter increasing according to the square of the bound nitrogen content. Oxygen partial pressure and point flame temperature are strong determinants of NO_x yield.

Table E4-7 presents comparative emissions for natural gas and fuel oils for 10^6 Btu heat release. The AP-42-based

TABLE E4-5. EMISSION FACTORS FOR NATURAL GAS COMBUSTION

	Industrial Process Boiler	
Pollutant	$lb/10^6 ft^3$	$kg/10^6 m^3$
Particulates	5 - 15	80 - 240
Sulfur Oxides (SO_2)[a]	0.6	9.6
Carbon Monoxide	17	272
Hydrocarbons (as CH_4)	3	48
Nitrogen Oxides (NO_2)	(120 - 230)[b]	(1920 - 3680)[b]

[a] Based on an average sulfur content of natural gas of 2,000 $g/10^6$ std ft^3 (4,600 $g/10^6$ N m^3).

[b] This represents a typical range for many industrial boilers. For large industrial units (100 MM Btu/hr), the NO_x factors presented for power plants are used.

Source: Reference 18.

TABLE E4-6. EMISSION FACTORS FOR FUEL OIL COMBUSTION IN INDUSTRIAL BOILERS[a]

	Grade of Oil			
	Residual oil		Distillate oil	
Pollutant	lb/10^3 gal	kg/10^3 liter	lb/10^3 gal	kg/10^3 liter
Particulate[b]	c	c	2	0.25
Sulfur dioxide[d]	157S	19S	142S	17S
Sulfur trioxide[d]	2S	0.25S	2S	0.25S
Carbon monoxide[e]	5	0.63	5	0.63
Hydrocarbons (total, as CH_4)[f]	1	0.12	1	0.12
Nitrogen oxides (total, as NO_2)	60[g]	7.5[g]	22	2.8

[a] Industrial boilers can be classified, roughly, according to their gross (higher) heat input rate as >15 x 10^6, but <250 x 10^6Btu/hr

[b] Particulate is defined as that material collected by EPA Method 5 (front half catch).

[c] Particulate emission factors for residual oil combustion are best described, on the average, as a function of fuel oil grade and sulfur content, as shown below.

Grade 6 oil: lb/10^3 gal = 10(S) + 3
Where: S is the percentage (by weight) of sulfur in the oil
Grade 5 oil: 10 lb/10^3 gal
Grade 4 oil: 7 lb/10^3 gal

[d] S is the percentage (by weight) of sulfur in the oil.

[e] Carbon monoxide emissions may increase by a factor of 10 to 100 if a unit is improperly operated or not well maintained.

[f] Hydrocarbon emissions are generally negligible unless unit is improperly operated or not well maintained, in which case emissions may increase by several orders of magnitude.

[g] Nitrogen oxides emissions from residual oil combustion in industrial boilers are strongly dependent on the fuel nitrogen content and can be estimated more accurately by the following empirical relationship:

$$\text{lb } NO_2/10^3 \text{ gal} = 22 + 400\,(N)^2$$

Where: N is the percentage, by weight, of nitrogen in the oil. Note: For residual oils having high (>0.5%, by weight) nitrogen contents, one should use 120 lb $NO_2/10^3$ gal as an emission factor.

Source: Reference 19

TABLE E4-7. REFINERY FUEL EMISSIONS AT EQUIVALENT HEAT RELEASE

FUEL TYPE	NATURAL GAS(a)	#2 F.O.(b)	#6 F.O.(b)
Gross Heating Value	1012 Btu/ft^3 (c)	19,460 Btu/lb(d)	18,200 Btu/lb(d)
Specific Gravity	0.55/Air	0.856/water	0.972/water(d)
Amount Equivalent to 10^6 Btu heat release	988 ft^3	7.20 gal	6.78 gal
Emissions lb per 10^6 Btu:			
SO_2: NSPS	2.66×10^{-3} (e)		
SO_2: (av)	5.9×10^{-4}	0.306	2.13
Particulates (av)	9.9×10^{-3}	0.014	0.16
CO	1.68×10^{-2}	0.036	0.034
HC	3.0×10^{-3}	7.2×10^{-3}	6.8×10^{-3}
NO_x (av)	0.17	0.16	0.41
Sulfur Wt% (oils only)		0.3 (typical)	2.0 (high)(f)

(a) Reference 20

(b) Reference 21

(c) Accepted value for pure methane

(d) Reference 22

(e) NSPS emission limit of SO_2 =

$$\frac{0.1 \text{ gr } H_2S}{10 \text{ ft}^3 \text{ nat. gas}} \times \frac{64 \text{ lb } SO_2}{34 \text{ lb } H_2S} \times \frac{1 \text{ lb}}{7000 \text{ gr}}$$

$$= 2.69 \times 10^{-6} \frac{\text{lb } SO_2}{\text{ft}^3 \text{ nat. gas}}$$

(f) Residual fuel oil sulfur levels range from 0.3 Wt. percent (N.Y. City) to 2.0 percent (Midwest) according to sales data as regularly published in Oil and Gas Journal.

"average" natural gas contains only about 22 percent of the sulfur equivalent allowed by NSPS (0.10 grain/10 ft^3 gas) (Column 1). Fuel oils containing 0.3 - 2.0 weight percent sulfur, which represent the broad range of sulfur levels in fuels, emit from 500 to 3,600 times as much SO_x as the "average" natural gas. Particulates from No. 2 oil are estimated to be only 1.4 times that of natural gas, but No. 6 fuel oil emits about 16 times as much.

Carbon monoxide and hydrocarbon emissions at identical heat release are about two times higher for fuel oils than for natural gas; nitrogen oxides emissions for gas and No. 2 fuel oil are about equal and smaller than No. 6 fuel oil NO_x emissions by a factor of 2.6.

Over all, the substitution of fuel oils for natural gas without instituting additional controls will have a detrimental impact on the environment.

4.3 Hydroprocessing as Feedstock Pretreatment

Hydroprocessing includes those processes in which hydrogen is combined with a feedstock and passed over a catalyst at elevated temperature and pressure. There are three categories of hydroprocessing, depending on the severity of the process: (1) hydrocracking, in which 50 percent or more of the feed is reduced in molecular weight; (2) hydrorefining, in which 10 percent or less of the feed is reduced in molecular weight; and (3) hydrotreating, in which essentially no reduction in molecular weight occurs.

Though all three types of processes are used to clean feedstocks, the main purpose of hydrocracking is the making of new products; therefore it is not discussed further in this section. Hydroprocessing of products (such as lube oils) is also not discussed here, even though such treatment may contribute to reduced emissions when the products are used. Hydrorefining and hydrotreating of feedstocks to be subjected to further processing are included in this section.

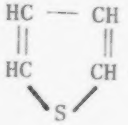
Some examples of hydroprocessing as feedstock pretreatment are:

- hydrodesulfurization of residual feedstock to be used in fuel oil production or catalytic cracking;
- hydrodesulfurization of heavy gas oils and middle distillates to be used in the production of jet fuels, diesel fuels, and heating oils;
- hydrodesulfurization of heavy gas oils to be used as high-quality catalytic cracking feed;
- hydrodesulfurization and hydrodenitrogenation of naphtha and straight-run crude distillate streams to be used as primary feeds for the isomerization and catalytic reforming units.

These and other uses of hydroprocessing are discussed more thoroughly in Section 4.4 of Appendix F.

Hydroprocessing removes sulfur- and nitrogen-containing compounds, the heavy metals, oxygen, and halides. Hydrotreating also stabilizes unsaturated hydrocarbons by saturating the double bonds. Typical reactions for these operations are given in Table E4-8.

TABLE E4-8. TYPICAL HYDROPROCESSING REACTIONS

Desulfurization:	
Mercaptans:	$RSH + H_2 \rightarrow RH + H_2S$
Sulfides:	$R_2S + 2H_2 \rightarrow 2RH + H_2S$
Disulfides:	$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$
Thiophenes:	 $+ 4H_2 \rightarrow C_4H_{10} + H_2S$
Denitrogenation:	
Pyrrole:	$C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3$
Pyridine:	$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$
Deoxidation:	
Phenol:	$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O$
Peroxides:	$C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O$
Dehalogenation:	
Chlorides:	$RCl + H_2 \rightarrow RH + HCl$
Hydrogenation:	
Pentenes:	$C_5H_{10} + H_2 \rightarrow C_5H_{12}$

Source: Reference 22.

Desulfurization requires less severe operating conditions that does nitrogen removal. Sulfur removal is less difficult for paraffins than naphthenes and aromatics.[21]

Hydrogen consumption is also less for sulfur removal than for nitrogen removal: about 70 scf/bbl feed/percent sulfur compared to about 320 scf/bbl feed/percent nitrogen. About 180 scf of hydrogen are required per barrel of feed per percent removal of oxygen. Hydrogen consumption increases rapidly if cracking occurs. About two to ten times the stoichiometric hydrogen are actually required because of hydrogen dissolving in the oil.[22]

A number of catalysts have been used for hydroprocessing, including cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide. Cobalt and molybdenum oxides or alumnia are used most commonly, but nickel-cobalt-molybdenum or nickel-molybdenum compounds or alumina are more efficient if nitrogen removal is a significant factor.[22]

Catalyst consumption varies from 0.001 to 0.007 lb/bbl feed, depending on the severity of the operation, the gravity of the feed, and the metals content of the feed.[22] The deposition of metals from the feed onto the catalyst can be a major problem, especially with residual feeds. The catalyst should be capable of remaining active even with accumulated metals. It should also be cheap enough to be thrown away after a single cycle, since deposited metals sometimes make regeneration unattractive.[23]

The overall impact of hydroprocessing is generally beneficial for reducing emissions. Removal of objectionable materials, besides reducing emissions from subsequent processes, can significantly reduce catalyst poisoning and equipment corrosion and can also increase yields. Hydrodesulfurization of catalytic cracking unit feeds is a very effective method for reducing sulfur emissions from catalytic cracking catalyst regeneration.

4.4 References

1. Stover, R. D. Control of Carbon Monoxide Emissions from FCC Units by Ultracat Regeneration. In: Ind. Process Ses. for Poll. Control, Proc. of the AIChE Workshop, 6:80-85, 1975.

2. Rheume, L., et al. Two New Carbon Monoxide Oxidation Catalysts Get Commercial Tests. Oil & Gas J., 74(21):66-70, 1976.

3. Rheume, L., et al. New FCC Catalysts Cut Energy and Increase Activity. Oil & Gas Journal, 74(20):103-110, 1976.

4. Davis, J. C. FCC Units Get Crack Catalysts. Chem. Eng., 84(12):77-79, 1977.

5. American Petroleum Institute, Refining Department, Proceedings of the 41st Mid-Year Meeting, Am. Pet. Inst. Ref. Dept., Washington, D.C. 1976.

6. Hartzell, F. D. and A. W. Chester. FCCU Gets a Catalyst Promoter. Hydrocarbon Process., 58(7):137-140, 1979.

7. Vasalos, I. A., et al. New Cracking Process Controls FCCU SO_x. Oil Gas J., 75(26):141-148, 1977.

8. New Catalyst Cuts FCC Sulfur Oxides 80-90 Percent. Oil Gas J.,75(13):38-39, 1977.

9. American Petroleum Institute, Division of Refining. Manual on Disposal of Refinery Wastes, Volume on Atmospheric Emissions. API Publ. 931. Washington, D.C., 1976.

10. Iya, K. S. Reduce NO_x in Stack Gases. Hydrocarbon Process., 51(11):163, 1972.

11. Reed, R. D. How to Cut Combustion-Produced NO_x. Oil Gas J., 72(3):63-64, 1974.

12. 1978 Refining Process Handbook, Cracking. Hydrocarbon Process, 57(1):107-111, 117-120, 1978.

13. Mason, H. F. and R. S. Tolberg. Hydrogen Processing--Clean Routes to Clean Products. AIChE Symp. Ser., 71(148):222, 1975.

14. Stupin, W. J. Thermally coupled Distillation--A Case History. Chem. Eng. Prog., 68(10):71, 1972.

15. Smith, D. E.,et al. Distill with Composition Control. Hydrocarbon Process., 57(2):99, 1978.

16. Null, H. R., D. E. Steinmeyer, and R. J. Larson. Process Design for Energy Conservation, Seminar Papers. AIChE Today Series. AIChE, New York, 1975.

17. Mix, J. J.,et al. Energy Conservation in Distillation. Chem. Eng. Prog., 74(4):49, 1978.

18. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division. Compilation of Air Pollutant Emission Factors. 3rd edition, AP-42. Research Triangle Park, North Carolina, August, 1977.

19. Gary, J. J. and G. H. Handwerk. Petroleum Refining, Technology and Economics. Marcel Dekker, New York, 1975.

20. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division. Compilation of Air Pollutant Emission Factors. 3rd edition, AP-42. Research Triangle Park, North Carolina, April, 1977.

21. Environmental Protection Agency, Office of Air Quality Planning and Standards, Monitoring and Data Analysis Division. Compilation of Air Pollutant Emission Factors. 3rd edition, AP-42. Research Triangle Park, North Carolina, May 1974.

22. Steam, 39th Edition. Babcock and Wilson, 1978, p. 5-17.

23. McKinney, J. D. and J. Stipanovich. Gulf HDS Handles Resids. Hydrocarbon Process., 50(5):97-102, 1971.

5.0 CONVERSION FACTORS

To Convert From	To	Multiple By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
$lb/10^6$ Btu	g/Mcal	18.0
$grain/ft^3$	g/m^3	2.29
$gal/10^6ft^3$	$ℓ/10^6m^3$	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mg/ℓ	119.8